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AN EFFICIENT NUMERICAL METHOD FOR STIRRED REACTOR CALCULATIONS

I. T. Osgerby

ARO, Inc.

November 1972

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FOREWORD

The work reported herein was sponsored by the Air Force Office of Scientific Research (AFOSR), under Grant AFOSR-PO-72-0001, Project 9711, and the Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), under Program Element 61102F, Project 9711. The project was monitored by Dr. B. T. Wolfson of the Air Force Office of Scientific Research.

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This technical report has been reviewed and is approved.

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ABSTRACT

An efficient method is presented for calculating chemical composition in a perfectly stirred reactor at a given pressure, stoichiometry, and mass flow per unit volume. Either temperature or enthalpy may be prescribed as the additional condition for the computations. By employing linearization techniques, the nonlinear equations of detailed finite rate chemical kinetic schemes are reduced to a system of algebraic equations which are solved iteratively. No difficulties are experienced in obtaining converged solutions using the techniques described in this report. A computer program is presented for solution of problems with arbitrary fuel/oxidant combinations.

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NOMENCLATURE

A_j	Pre-exponential coefficient in the j th reaction rate constant
$a_{k,\ell}$	The k th specie coefficient in the conservation equation for the ℓ th specie
B_j	Back reaction rate of the j th reaction
b_j	Back reaction rate constant in the j th reaction
C_ℓ	Constant in the ℓ th conservation equation
C_p	Specific heat of the mixture
C_{p_i}	Specific heat of species i
d_{ij}	Third-body efficiency of species i in the j th reaction
E_j	Activation energy in the j th reaction rate constant
F_i°	Standard molar free energy of species i
ΔF_j	Change in free energy in the j th reaction
f_j	Forward reaction rate constant in the j th reaction
H	Specific enthalpy of the mixture
\dot{H}_L	Enthalpy lost from the system
h_i	Specific enthalpy of species i
K_j	Equilibrium constant for the j th reaction
K_{p_j}	Equilibrium constant for the j th reaction (pressure units)
\dot{m}	Mass flow rate into the reactor
N	Number of linearly independent species
NR	Number of reactions
NT	Total number of species
P	Pressure
R	Universal gas constant (thermal units)

R'	Universal gas constant (pressure/volume units)
T	Temperature
t	Time
V	Volume of reactor
W	Molecular weight
X_j	Third body in a dissociation reaction
x_{ij}	Coefficient in the solution matrix
y_i	Constant in the solution matrix
a''_{ij}, a'_{ij}	Stoichiometric coefficients for the i th species in the j th reaction
β_j	Index which is zero for second-order and unity for third-order reactions
γ_i	Mole mass ratio of species i in the reactor
$\dot{\gamma}_i$	Rate of production of species i due to chemical reaction
δ_i	Finite approximation to the error in assumed species mole mass ratio
δ_T	Finite approximation to the error in assumed temperature in the reactor
ρ	Density of the gas mixture
τ_R	Residence time in reactor (average value for all molecules)

SUPERSCRIPTS

o	Denotes standard value or feed quantity
$*$	Denotes approximate value of a variable

SUBSCRIPTS

i, k, ℓ	Dummy subscripts on species
j	Denotes reaction number
T	Denotes temperature coefficient

SECTION I INTRODUCTION

A well-stirred reactor is a device into which fuel and oxidant are injected, mixed, and reacted. If the mixing time is much shorter than the total residence time in the reactor, then the temperature and composition in the device may be considered perfectly stirred, i.e., uniform and the same as the exhaust from the device.

The concept of a well-stirred reactor was initially developed by Longwell and co-workers (Refs. 1 through 3) for investigation of reaction fuel/oxidant systems. Typically, measurements were made of injection rates that caused extinction of the flame for various fuels, equivalence ratios, pressures, and initial temperatures. These measurements were used to deduce maximum volumetric rates for the aggregate of the participating reactions, i.e., the "volumetric-heat-release rates." Their lead has been followed by several groups of workers, namely: Clarke, et al (Refs. 4 through 6), Hottel, et al (Refs. 7 and 8). A large volume of literature exists in the chemical process industry where the stirred reactor is used extensively. It is in this industry where stirred reactor theory was extended to more than a one-step reaction from reactants to products and, in particular, incorporation of statistical models of turbulence and effects of incomplete mixing/stirring (Refs. 9 through 11). Jenkins and Yumlu (Ref. 12) introduced the concept of making detailed reaction rate studies with a stirred reactor. Detailed numerical studies were carried out for the hydrogen/oxygen system, using a program developed by Jones (Ref. 13) for solving the finite rate chemical kinetic equations. The computer program was used to determine corrections to reaction rate constants so that predicted flame temperatures could be made to agree with measured values for a limited range of operating conditions.

The strong similarity of a stirred reactor to the gas turbine engine primary combustor has led to its application to gaseous pollutant studies (Refs. 14 through 16). However, the large number of variables, 13 species plus temperature even for methane combustion, demanded a high degree of sophistication in iterative techniques to obtain solutions. Several solution techniques have been developed (Refs. 13 and 16). The method of Ref. 13 is based on solving a set of nonlinear algebraic equations which describe the chemical kinetics of a fuel/oxidant system. The equations are linearized about the solution and an iterative procedure used to obtain converged solutions. A similar technique is described in this report including extension to variable temperature as well as specie composition. The method used in Ref. 16 is referred to as a technique for solving the time dependent form of the stirred reactor equations by a relaxation method. Another method employs numerical integration techniques with the time dependent term in the stirred reactor equations relaxed to zero when the solution is obtained. Considerable difficulty has been experienced with the iterative method of solving the linearized algebraic equations. The equations are highly nonlinear and the generally used Newton-Raphson technique requires an approximate solution from which to start the iteration. The difficulty increases rapidly as the number of variables increases. The convergence problem becomes quite severe in chemical laser calculations where each excited state of a specie is considered as a separate specie (Ref. 17). The perfectly stirred reactor may constitute an ideal chemical laser because of the uniformity of chemical state over the whole volume and its ability to operate steady state as far from chemical equilibrium as desired (providing flameout does not occur).

The technique and program presented in this report have been used for a variety of problems over a large range of input pressures, temperatures, stoichiometries, and mass flows/unit volume. Convergence is obtained without difficulty even for large numbers of variables, and parametric calculations have been carried out with very short computational time requirements.

The system of equations to be solved and the method of solution is described. A listing of the program and a description is then given with representative sample calculations for a hydrogen/air and a methane/air system.

SECTION II

THEORY OF THE IDEAL STIRRED REACTOR WITH FINITE RATE CHEMISTRY

Suppose that a reactant gas stream flows at a mass flow rate (\dot{m}) into a reactor of volume V , its composition being defined by a set of values (γ_i^0), representing the inlet concentration of the component species i . The composition in the reactor is assumed uniform (perfectly stirred) and identical with that in the exhaust stream; it is defined by the set of values (γ_i). The temperature T is also supposed uniform in the reactor and exhaust stream. The reactor walls are assumed to be entirely inert chemically and do not catalyze the reactions in any way. The gases are assumed to be thermally perfect.

Conservation equations can be written as follows:

Species i

$$\frac{\dot{m}}{\rho V}(\gamma_i^0 - \gamma_i) + \dot{\gamma}_i = \frac{d\gamma_i}{dt} \quad (1)$$

The species production rate ($\dot{\gamma}_i$) is obtained from

$$\dot{\gamma}_i = \sum_{j=1}^{NR} (\alpha_{ij}'' - \alpha_{ij}') (F_j - B_j) \quad (2)$$

Energy

$$\frac{\dot{m}}{\rho V} \sum_{i=1}^{NT} (\gamma_i^0 h_i^0 - \gamma_i h_i) = \frac{dH}{dt} + \dot{H}_L \quad (3)$$

For steady-state, adiabatic operation, these equations reduce to those of Ref. 12:

$$\frac{\dot{m}}{\rho V}(\gamma_i^0 - \gamma_i) + \dot{\gamma}_i = 0 \quad (4)$$

$$\dot{H}_L = 0$$

The a''_{ij} and a'_{ij} are stoichiometric coefficients in the j th chemical reaction, F_j is the rate of the forward reaction, and B_j is the rate of the backward reaction. The quantities h_i and h'_i are specific enthalpies (functions of temperature only) in the reactor and inlet stream, respectively, of species i . The steady-state form of the equations is used in this report.

The reaction rates are related to the concentrations in the reactor by

$$F_j = f_j X_j \beta_j \prod_{i=1}^{NT} (\rho \gamma_i)^{a'_{ij}} \quad \text{and} \quad B_j = b_j X_j \beta_j \prod_{i=1}^{NT} (\rho \gamma_i)^{a''_{ij}} \quad (5)$$

where ρ is the density of the gas mixture in the reactor, f_j and b_j are rate constants of the forward and backward reactions, respectively, and X_j is a third body in a dissociation reaction and is given by

$$X_j = \sum_{i=1}^{NT} d_{ij} \gamma_i \quad (6)$$

where the d_{ij} represent third-body efficiencies. The rate constants are of the form

$$f_j = A_j T^{n_j} \exp(-E_j/RT) \quad (7)$$

however, the back reaction rate constant is not chosen independently. The rate constants obey the following relation:

$$b_j = f_j K_j \quad (8)$$

$$K_j = K_{p_j} (R' T)^{\sum_{i=1}^{NT} (a'_{ij} - a''_{ij})} \quad (9)$$

$$K_{p_j} = \exp(-\Delta F_j/RT) \quad (10)$$

$$= \exp \left[- \sum_{i=1}^{NT} (a''_{ij} - a'_{ij}) F_i^0 / RT \right] \quad (11)$$

K_j is the equilibrium constant and F_i^0 is the molar free energy of species i . The system of equations is completed with the equation of state

$$P = \rho \frac{R'}{W} T = \rho R' T \sum_{i=1}^{NT} \gamma_i \quad (12)$$

where P is the system pressure and W is the molecular weight of the gas mixture.

The equations form a complete algebraic system of nonlinear equations for steady-state operating conditions and can be solved by standard techniques once a reaction kinetic

scheme, rate data, and thermodynamic data are given. An efficient method of solution is described which has proved quite successful for a large range of problems.

It is assumed that at least one approximate solution can be obtained using an equilibrium composition calculation, a one-dimensional finite rate chemistry calculation (plug flow) or solution by integration of the transient stirred reactor Eq. (1) with the transient term relaxed to zero. Guessing a solution is nearly impossible for all but very simple reaction schemes such as that of Ref. 12.

These approximate values (γ_i^*) and T^* are used in a Newton-Raphson procedure to obtain first-order correction terms from which new values of γ_i and T can be obtained

$$\gamma_i = \gamma_i^* + \delta_i \quad (13)$$

$$T = T^* + \delta_T \quad (14)$$

By repeating the procedure, the δ_i and δ_T can be relaxed to some negligible value; thus final values (solutions) for γ_i and T are obtained.

The correction equations are obtained as follows:

$$\gamma_i = \gamma_i^* + d\gamma_i \quad \text{and} \quad \dot{\gamma}_i = \dot{\gamma}_i^* + d\dot{\gamma}_i \quad (15)$$

$$d\gamma_i = \frac{\partial \gamma_i^*}{\partial T} dT + \frac{\partial \gamma_i^*}{\partial \rho} d\rho + \sum_{k=1}^{NT} \frac{\partial \gamma_i^*}{\partial \gamma_k} d\gamma_k \quad (16)$$

$$dF_j = \frac{\partial F_j^*}{\partial T} dT + \frac{\partial F_j^*}{\partial \rho} d\rho + \sum_{k=1}^{NT} \frac{\partial F_j^*}{\partial \gamma_k} d\gamma_k \quad (17)$$

$$dB_j = \frac{\partial B_j^*}{\partial T} dT + \frac{\partial B_j^*}{\partial \rho} d\rho + \sum_{k=1}^{NT} \frac{\partial B_j^*}{\partial \gamma_k} d\gamma_k \quad (18)$$

$$dX_j = \sum_{k=1}^{NT} \frac{\partial X_j^*}{\partial \gamma_k} d\gamma_k \quad (19)$$

Not all variables are linearly independent; thus,

$$d\rho = \frac{\partial \rho^*}{\partial T} dT + \sum_{k=1}^{NT} \frac{\partial \rho^*}{\partial \gamma_k} d\gamma_k \quad (20)$$

$$d\gamma_\ell = \sum_{k=1}^N a_{k,\ell} d\gamma_k \quad \ell = N + 1, NT \quad (21)$$

$$\gamma_\ell = C_\ell + \sum_{k=1}^N a_{k,\ell} \gamma_k \quad (22)$$

The C_ℓ values are obtained from element conservation equations.

The partial derivatives are obtained from the preceding conservation equations. If temperature is an unknown variable, the energy equation is used to obtain a correction equation for it:

$$H = \sum_{i=1}^{NT} \gamma_i h_i \quad (23)$$

$$dH = \sum_{i=1}^{NT} \gamma_i dh_i + \sum_{k=1}^N \left(h_k + \sum_{\ell=N+1}^{NT} a_{k,\ell} h_\ell \right) dy_k \quad (24)$$

$$= C_p dT + \sum_{k=1}^N \left(h_k + \sum_{\ell=N+1}^{NT} a_{k,\ell} h_\ell \right) dy_k \quad (25)$$

where

$$C_p = \sum_{i=1}^{NT} \gamma_i C_{p,i} \quad (26)$$

Summarizing gives

$$\dot{\gamma}_i = \dot{\gamma}_i(\gamma_k, T) \quad i,k = 1, N \quad (27)$$

$$\rho = \rho(\gamma_k, T) \quad (28)$$

$$\gamma_\ell = \gamma_\ell(\gamma_k, T) \quad \ell = N+1, NT \quad (29)$$

$$\gamma_i^o - \gamma_i^* + r_R^* \dot{\gamma}_i^* = dy_i - r_R^* d\dot{\gamma}_i - \dot{\gamma}_i^* dr_R \quad (30)$$

where

$$r_R = \frac{\rho V}{m} \approx r_R^* + dr_R \quad (31)$$

and

$$\frac{dr_R}{r_R} = \frac{d\rho}{\rho} \quad (32)$$

Substituting for dr_R gives

$$\gamma_i^o - \gamma_i^* + r_R^* \dot{\gamma}_i^* = dy_i - r_R^* \left[\dot{\gamma}_i^* + \frac{\dot{\gamma}_i^*}{\rho^*} \left(\frac{\partial \rho^*}{\partial T} dT + \sum_{k=1}^{NT} \frac{\partial \rho^*}{\partial \gamma_k} dy_k \right) \right] \quad (33)$$

Substituting for $d\dot{\gamma}_i$ and dy_i

$$\begin{aligned} \gamma_i^o - \gamma_i^* + r_R^* \dot{\gamma}_i^* &= dy_i - r_R^* \left[\frac{\partial \dot{\gamma}_i^*}{\partial T} - \frac{\dot{\rho}^*}{T^*} \left(\frac{\partial \dot{\gamma}_i^*}{\partial \rho} + \frac{\dot{\gamma}_i^*}{\rho^*} \right) dT \right] \\ &\quad - r_R^* \left\{ \sum_{k=1}^N \left[\left(\frac{\partial \dot{\gamma}_i^*}{\partial \gamma_k} - \rho^* W^* \frac{\partial \dot{\gamma}_i^*}{\partial \rho} \right) \right. \right. \\ &\quad \left. \left. + \sum_{\ell=N+1}^{NT} a_{k,\ell} \left(\frac{\partial \dot{\gamma}_i^*}{\partial \gamma_\ell} - \rho^* W^* \frac{\partial \dot{\gamma}_i^*}{\partial \rho} \right) \right] \right. \\ &\quad \left. \left. - \dot{\gamma}^* W^* \left(1 + \sum_{\ell=N+1}^{NT} a_{k,\ell} \right) \right] dy_k \right\} \end{aligned} \quad (34)$$

where

$$\frac{\partial \rho^*}{\partial T} = - \frac{\rho^*}{T^*}$$

and

$$\frac{\partial \rho^*}{\partial \gamma_k} = - \rho^* W^* \quad (35)$$

2.1 METHOD OF SOLUTION

When a converged solution is obtained both the left- and right-hand sides of Eq. (34) are approximately equal to zero. By using the Newton-Raphson technique, estimates (γ_i^*) for N of the total number of species NT are required together with an estimate of the temperature (T^*). These estimates are used to evaluate the terms on the right-hand side of Eq. (34). Thus, a matrix can be formed as follows:

$$y_i = \sum_{k=1}^N x_{i,k} \delta_k + x_{i,T} \delta_T \quad i = 1, N \quad (36)$$

where $d\gamma_k$ is replaced by the finite approximation (δ_k), dT is replaced by δ_T , y_i represents the left-hand side of Eq. (34), and the x_{ik} represent the coefficients on the right-hand side. The $(N + 1)$ row of coefficients to be added to the above matrix are:

$$y_{N+1} = dH \approx \Delta H = H_o - H \quad (37)$$

$$x_{N+1,k} = h_k + \sum_{\ell=N+1}^{NT} a_{k,\ell} h_{\ell} \quad (38)$$

Thus,

$$y_{N+1} = \sum_{k=1}^N x_{N+1,k} \delta_k + C_p \delta_T \quad (39)$$

If the stirred reactor composition is required at a specified temperature and pressure, instead of in terms of the inlet energy and pressure, then only the coefficients of an $N \times N$ matrix are required, and the δ_T terms are ignored.

The matrix is solved for the unknown δ_k and δ_T , and values of $\gamma_k = \gamma_k^* + \delta_k$ and $T = T^* + \delta_T$ are computed. The process is repeated until $\delta_k \ll \gamma_k$ and $\delta_T \ll T$.

Some difficulty was experienced in obtaining converged solutions for $N > 6$. The primary problem was found to be the exponential response of specie derivative terms when large temperature corrections were required in constant enthalpy calculations. This problem was overcome by deleting all temperature coefficients from the matrix and allowing several composition iterations to be made between each temperature correction obtained as follows:

Let

$$H_o - H = C_p \Delta T$$

H and C_p are evaluated from the current value of γ_i^* and T^* , and a new value of T is given by

$$T = T^* + \Delta T \approx T^* + (H_o - H)/C_p$$

It was also found that if an odd fraction was used to multiply each indicated correction for species and a large fraction used to reduce the temperature correction until the ΔT changed sign and then use a small fraction to reduce it, oscillations about the solution were eliminated.

2.2 REACTION RATE SENSITIVITY COEFFICIENTS

The experiments described in Ref. 12 were designed to furnish data to allow adjustment of the reaction rates so that the reactor temperature predicted by the computer program could be made to agree with the measured value. An analysis of the sensitivity of predicted reactor temperature to individual reaction rate constants was carried out to determine which, if any, had a dominant role in determining the reactor temperature. Since reaction rates are functions of composition also, the calculations were repeated with different values of initial water concentration in the feed of hydrogen/oxygen. The sensitivity coefficient is defined as

$$f_j \frac{\partial T}{\partial f_j}$$

with units of $^{\circ}\text{K}$. It represents the change in reactor temperature for an infinitesimal change in reaction rate constant (f_j). The quantity is evaluated numerically for an 0.1-percent increase in reaction rate constant (f_j):

$$f_j \frac{\partial T}{\partial f_j} \approx f_j \frac{\Delta T}{\Delta f_j}$$

This calculation is carried out for each reaction rate in sequence. The sensitivity to initial feed composition may also be evaluated with the computer program. Control integers are incorporated whereby the feed composition of any variable is assigned multiples of 5 percent of the inert species composition. Reaction rate sensitivity coefficients are re-evaluated for each new feed composition. The range of possible experiments is considerably increased by this means since, for the methane/air system, CO , CO_2 , and H_2O can be readily included in the feed stream.

This subroutine is used to gain insight into which reactions are rate controlling for various reactor temperatures and feed compositions. Tabulating the sensitivity coefficients for a wide range of input conditions and reactor residence times shows whether some reactions may even be eliminated in practical calculations. If the sensitivity coefficient in a reaction is always small relative to others, then this reaction could probably be eliminated. An example is discussed in a later section for the methane/air system. An example for the hydrogen/oxygen/steam system is given in Ref. 12.

SECTION III

COMPUTER PROGRAM

A computer program was written for the Raytheon 520 digital computer in Fortran IV language. A listing of the program is given in Appendix III. The program is written in a general format so that any chemical system can be investigated. The maximum number of different species is 20, and the maximum number of chemical reactions is 76. Either of these numbers can be readily increased or decreased as desired.

A number of options are included which allow a range of known flame temperatures and/or a range of mass flows per unit volume to be used. An additional subroutine has been incorporated to calculate temperature sensitivity coefficients for reaction kinetic schemes.

The program is divided into several subroutines which execute specific parts of the overall calculation. The calculations are controlled by integer variables defined in the main program. Some comments have been added to help identify the types of calculations carried out in the program.

3.1 MAIN PROGRAM

Data cards are as follows:

- I. P, T, TO, DELT, TMIN
- II. MDOTV, DMDV, NT, N, LT, MT, IT, NR, NN, NNT
- III. XO(I), I = 1, NT
- IV. X(I), I = 1, NT
- V. W(I), I = 1, NT

I. P is the system pressure (atm), T is the known or estimated flame temperature (°K), TO is the feed temperature, DELT is the temperature decrement desired when temperature is not a variable, and TMIN is the minimum temperature at which a calculation is to be attempted.

II. MDOTV is the mass flow per unit volume ($\text{g cm}^{-3} \text{ sec}^{-1}$), DMDV is the factor by which MDOTV is to be increased (or decreased) in parametric calculations, NT is the total number of chemical species, N is the number of linearly independent species, LT is the number of times MDOTV is to be multiplied by DMDV, MT is the number of times DELT is to be subtracted from T, IT is a control variable (=1 for constant temperature, and =2 for constant enthalpy calculations). NR is the total number of chemical reactions, NN is a control variable (=0 to bypass the reaction rate sensitivity calculation and =1, the species number whose concentration is to be changed in the reaction rate sensitivity calculations), and NNT is the number of times species NN is to be changed.

III. $XO(I)$ is the molar ratio of species I in the feed. The order of the species is not arbitrary; the species to be evaluated with conservation equations must be last.

IV. $X(I)$ is the molar ratio of species I in the reactor. The order of the numbers must be the same as in the card above. This requirement applies to all species and species data cards.

V. $W(I)$ is the gram-molecular weight of species I.

Calculations carried out in the main program are:

- i. normalization of input concentrations followed by conversion to mole mass units and summed to obtain the reciprocal molecular weight of the mixture.
- ii. Subroutine BB3 is called. In this subroutine, species enthalpies, specific heats, free energies, and derivatives of free energies are evaluated. The first time BB3 is called, the initial enthalpy corresponding to the feed temperature and composition is calculated (HO). The next time BB3 is called, the current value of T is used. The subroutine is not called again until T is changed. The free energies and their temperature derivatives are used to evaluate equilibrium constants and their temperature derivatives.
- iii. Calculation of feed and estimated flame densities.
- iv. Calculation of estimated reactor residence time.

3.2 SUBROUTINE COMP

This subroutine calls a number of subroutines in which the data necessary to evaluate the coefficients for the iteration matrix are calculated. When the coefficients have been evaluated, a matrix reduction routine is called which returns the values of the corrections to the initial estimates. A check is then made to determine whether the largest correction would produce a negative species concentration, if so then all correction terms are reduced by the amount necessary to prevent this, and finally the corrections are multiplied by 0.37. This has ensured satisfactory convergence for all calculations attempted. The new values of the species are evaluated, and a check is made to see if the original equations are satisfied; if so, the converged solutions are used to compute final values of molecular weight, density, and enthalpy and these values are returned to the main program.

The sequence of calculation is as follows:

- i. Subroutine BB1 is called once only, to obtain coefficients for the conservation equations and their derivatives.
- ii. Subroutine BB4 is called every time a new set of composition corrections is to be calculated. This subroutine also calls Subroutine

RATES if the temperature is changed, otherwise once only to establish the values of the reaction rate constants and their derivatives. The majority of the partial derivatives are calculated in subroutine BB4.

- iii. The coefficients for the matrix are evaluated.
- iv. Subroutine CHOLES, the matrix reduction routine, is called to evaluate the values of the corrections.
- v. The corrections are used and convergence to the solution evaluated.

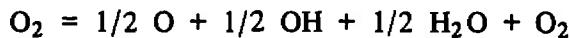
3.3 SUBROUTINE BB1

This subroutine evaluates the coefficients of the conservation equations using constants which are read in the first time the subroutine is called. The data are read in as follows:

I. $J(I)$, $I = NL$ where NL is the number of linearly dependent species ($NL = NT - N$). Each integer read in denotes how many coefficients are to be called for in the $J(I)$ th conservation equation.

II. $(NS(K,I), SC(K, I), K = 1, JJ), I = NL$ where $JJ (=J(I))$ is the number of species in each conservation equation. $NS(K, I)$ is the number of the species, and $SC(K, I)$ is the value of the coefficient in the conservation equation.

An example for conservation of H_2 and O_2 in the H_2/O_2 system is



Card I 4, 4

Card IIa 1, 0.5 3, 0.5 4, 1.0 5, 1.0

Card IIb 2, 0.5 3, 0.5 4, 0.5 6, 1.0

where 1 = H, 2 = O, 3 = OH, 4 = H_2O , 5 = H_2 , 6 = O_2 . The order of the cards must correspond to the order of the molecular weights in the main program.

3.4 SUBROUTINE BB3

This subroutine is used to calculate species enthalpy, specific heat, free-energy, and derivatives of free energy. The first time subroutine BB3 is called, a set of coefficients is read in as follows:

$C(I, KK), I = 1, 14 KK = 1, NT$

These coefficients correspond to those given in NASA-SP-3001 (Ref. 18). The first seven coefficients correspond to the temperature range from 300 to 1000°K and the second seven are for the range from 1000 to 5000°K, i.e., fourteen coefficients per specie. These data cards must correspond to the order of the molecular weights in the main program.

3.5 SUBROUTINE CHOLES

This is a standard matrix reduction routine developed by Glassman¹. It is based on the Choleski method for matrix factorization.

3.6 SUBROUTINE BB4

This subroutine contains the "chemical kinetics" of the chemical system being investigated. The data cards contain all the information relating to chemical reactions and reaction rate constants. Subroutine RATES is called first to evaluate reaction rates and reaction rate derivatives; then the partial derivatives required for the matrix reduction equations are evaluated.

The following nomenclature is used to denote the corresponding variables in Section III.

$$\begin{aligned} BO(I) &= \gamma_i^o & B(I) &= \gamma_i & R &= \rho & DBDB(I,K) &= \frac{\partial \dot{\gamma}_i}{\partial \gamma_k} \\ DBDT(I) &= \frac{\partial \dot{\gamma}_i}{\partial T} & DBDR(I) &= \frac{\partial \dot{\gamma}_i}{\partial \rho} & BD(I) &= \dot{\gamma}_i \end{aligned}$$

The reaction rate cards are read in as follows:

- I. NR
- II. ITR(IR), ITP(IR), (KK(IR, I), I = 1, 4), A(IR), EX(IR), TEX(IR), IE(IR), IC(IR), IB(IR)
- III. (I1(IR), ER(IR, I), I = 1, 4)
- IV. KS(IR, I), I = 1, IC (IR)

I. NR is the total number of reactions, IR is an integer in the range IR = 1, NR.

II. ITR(IR) and ITP(IR) are the number of reactants and products in the IRth reaction. KK(IR, I), I = 1, 4 denotes the Ith species in the IRth reaction, and a maximum of four is allowed (in a recombination reaction, e.g., H + H + M = H₂ + M, M has the value NT + 1 and the four integers corresponding to the reactants and products 1, 1, 5, 7 in the nomenclature of Subroutine BB1). A(IR) is the pre-exponential factor, EX(IR) is an activation energy, and TEX(IR) is a temperature exponent in the IRth reaction rate constant.

¹H. N. Glassman, Central Computer Operations, ARO, Inc., AEDC

IE(IR), IC(IR), and IB(IR) are integer controls for different types of reactions. They are most easily explained by the following examples:

a. Two body reaction with forward rate constant data read in:²



$$\text{IR} = 3, \text{A}(1) = 1.9 \times 10^{14}, \text{EX}(1) = 9007.0, \text{TEX}(1) = 0$$

$$\text{IE}(1) = 0, \text{IC}(1) = 0, \text{IB}(1) = 1$$

The data card for this reaction is

$$2, 2, 1, 6, 3, 2, 1.9E + 14, 9007., 0., 0, 0, 1$$

Cards III and IV are not required.

b. Three-body reactions must be written as recombination reactions:



If the known rate is k_b for the back reaction, then $\text{IB}(1) = -1$ so that the reaction rate corresponds to the right-hand side.

The card would then read

$$3, 2, 1, 1, 4, 7, 5.0E + 18, 0.0, -1.15, 0, 0, -1$$

c. Three-body reaction with H_2O 4.7 times as efficient as any other species acting as a third body: $\text{IR} = 8$ $\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$

Card II would read (with $\text{IE}(2) = 1$)

$$3, 2, 1, 3, 4, 7, 1.2E + 17, -252., 0., 1, 0, 1$$

Card III would read

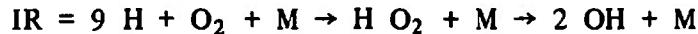
$$4, 3.7 \text{ where } \text{I1}(2) = 4 \text{ and } \text{ER}(2) = 3.7$$

The value of $\text{ER}(\text{IR})$ is always 1.0 less than the third-body efficiency. If they are all equal to unity, the card is not required. If the reverse reaction is effectively zero, then $\text{IB}(2) = 0$, and

Card II would read

$$3, 2, 1, 3, 4, 7, 1.2E + 17, -252., 0., 1, 0, 0$$

d. Special Reaction:



This reaction is handled with data given in Card IV.

²Reactions and rate data are detailed in Table I (Appendix II).

- II. 3, 2, 1, 6, 7, 2.1E + 18, 0., -1, 1, 5, 0
- III. 4, 2.6
- IV. 1, 6, 7, 3, 3

where IC(3) = 5, the number of molecules involved whose numbers are specified in Card IV. Card III is required since H_2O is assumed to be 3.6 times as efficient as all other molecules acting as third bodies.

3.7 SUBROUTINE RATES

This subroutine evaluates the values of the reaction rate constants and derivatives required in subroutine BB4.

In Section III, $f_j = A_j T^{n_j} \exp(-E_j/RT)$

in this subroutine $f_j = FR(IR) = A(IR) T^{TEX(IR)} e^{E(IR)/T}$

In Section III, $b_j = f_j K_j$ ($K_j = EQ$ in this subroutine).

This equilibrium constant EQ is evaluated using free energies obtained in Subroutine BB3.

3.8 SUBROUTINE RCHEK

Reaction rate sensitivity coefficients are obtained in this subroutine using a numerical approximation for

$$f_j \frac{\partial T}{\partial f_j}$$

The subroutine is called if the integer NN $\neq 0$ in the main program. If NN is nonzero, it is equal to the number of one of the constituent species.

The control integer NNT determines if and how many times the feed concentration of species NN is to be increased as a fixed percentage (5 percent of the last species concentration with the inert N_2 the species NT). This enables the sensitivity coefficients to be determined as a function of each species thought to be significant. Inclusion of the call statement for this subroutine within the loops for temperature and/or mass flows per unit volume enables the effect of temperature and residence time to be calculated also.

The sensitivity coefficient is evaluated as follows:

An integer (ICR) is specified and when subroutine rates is called, the pre-exponential coefficient A(IR) is relabelled A(ICR) and multiplied by 1.001. The calculation is carried out with IT = 2, i.e., at constant enthalpy and a new value of temperature determined and compared with the value calculated previously (before A(IR) was multiplied by 1.001).

The difference in these two temperatures is multiplied by 1000 and this represents the temperature change ΔT for a 0.1-percent change in reaction rate constant. The sequence is carried out for ICR = 1, (NR + 1), i.e., all the reactions are investigated including the (NR + 1)th, which is a check to see if $\Delta T = 0$. for this case.

This subroutine is useful for determining if certain reactions have a negligible effect on the chemical system ($\Delta T \approx 0$ for a range of stoichiometries, residence times, temperatures, etc.). If they are negligible, they can be eliminated to speed up the calculation and reduce computational time.

3.9 SAMPLE OUTPUT

The sample output data immediately after the listing are for a CH_4 /Air system detailed in the next section. The integer controls correspond to the use of subroutine RCHEK. Thermodynamic data evaluated at temperature T_0 °K are listed on the first page of output lists. The coefficients used in Subroutines BB1 and BB4 are listed on the second page. Solutions for the case $\gamma_{\text{CH}_3}^\circ$ (BO(6)) equals 0.0 and 0.5 percent of $\gamma_{\text{CH}_4}^\circ$ (BO(5)) are presented on the third page. The first solution is an IT = 1 case to determine the enthalpy at the given temperature and is written from the main program. The second solution (IT = 2) contains the sensitivity coefficients with the same feed as for the first solution and is written from Subroutine RCHEK. The third solution (IT = 2) is written from Subroutine RCHEK for $\gamma_{\text{CH}_3} = 0.005 \gamma_{\text{CH}_4}^\circ$.

SECTION IV SAMPLE CALCULATIONS AND DISCUSSION

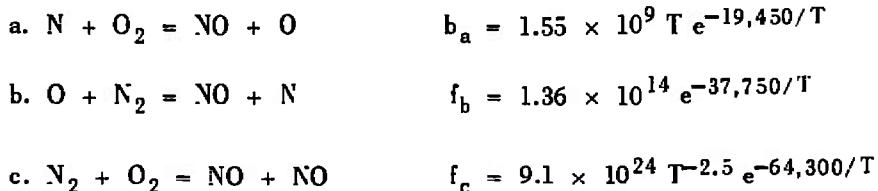
4.1 HYDROGEN/OXYGEN SYSTEM

The chemical kinetic scheme and reaction rate data used are given in Table I. Enthalpy versus temperature data are shown in Figs. 1a and b (Appendix 1) for equivalence ratios (ER) = 0.1 and 1.0. The minimum in each curve corresponds to the temperature at which the flame "blows out." The stirred reactor requires a significant rate of production of the "active" species H, O, OH, and H_2O to sustain a flame, and a minimum residence time is required for this to occur in the reactor. This is, of course, why the minimum shifts to higher temperatures as the residence time is decreased (increased m/v).

The chemistry in perfectly stirred reactors (PSR) differs somewhat from that in premixed plug flow reactors (PFR). In a PFR, the H, O, and OH species concentrations increase exponentially with time during the ignition process, followed by a decrease as the temperature increases to the flame temperature. In a PSR, the production rate of H, O, and OH is always positive as required by the species conservation equation. This requirement leads to different behavior with increasing time as shown in Figs. 2a through c. This characteristic may be used to advantage in a chemical laser where a supply of radicals is required in a chain-type reaction, operating marginally past the spontaneous ignition point (Ref. 17). The concentrations as a function of temperature with enthalpy constant in both reactor models are essentially identical as shown in Fig. 3 with numerical errors accounting for the difference. The PFR calculations were obtained with a separate computer program.

4.2 METHANE/AIR SYSTEM

The chemical kinetic and reaction rate data are given in Table II. Nitric oxide formation represents a composite of the following reactions:



The rate of production of NO is given by

$$\text{N}_2 + \text{O}_2 = 2 \text{NO} f = f_b, \text{ i.e., } \dot{\gamma}_{\text{NO}} = 2f_b y_{\text{N}_2} y_{\text{O}_2}$$

The error in NO concentration is small for temperatures $< 2500.0^{\circ}\text{K}$ and could be readily reduced with some numerical experimentation on the reverse reaction rate constant.

An enthalpy temperature map for this system is shown in Fig. 4. Some results obtained using the reaction rate check subroutine are shown in Table III.

The results are presented for a few calculations only. In practice, a comprehensive series of tables would be necessary with as large a range as possible of input conditions, composition, stoichiometry, and residence time (τ_R). Inspection of the table shows that the nitric oxide production equation could probably be eliminated from thermal balance calculations for this range of conditions since its sensitivity coefficient is always relatively small. It obviously should be retained if nitric oxide composition is to be estimated. A marked sensitivity of nearly all reactions is evident near the blowout condition (see Table III) for $m/V = 16$, $T = 1500^{\circ}\text{K}$. This table does not indicate any operating condition for which only one reaction has a high sensitivity coefficient. This is what one should look for in a comprehensive series of tables since this indicates that the reaction rate constant of this reaction can be adjusted to make predicted and experimental temperatures agree. Repeating the procedure for each experiment with one or more dominant reactions allows successive improvement of each rate constant to be made.

It should be remembered that the stirred reactor concept is limited to evaluating a given chemical kinetic and reaction rate scheme, i.e., it cannot serve as a source of fundamental data on individual chemical reactions. It can, however, be used (numerically) to evaluate the possible influence of proposed reactions. Thus, the stirred reactor provides a simple means of evaluating simplified schemes designed to approximate more detailed chemical kinetic schemes.

SECTION V CONCLUSIONS

The computer program has been used successfully to solve large sets of nonlinear equations in an efficient manner. No difficulties in obtaining solutions are experienced if the following directions are followed closely:

1. Obtain one set of concentrations from a finite rate solution or an equilibrium solution.
2. If temperature is to be varied, restrict the temperature change to less than 300°K. If larger temperature changes are desired, then the solution should be "marched" i.e., split up the desired change into a number of smaller changes.

The program allows the user to evaluate a chemical system parametrically from flameout to equilibrium with any desired pressure, temperature or enthalpy, feed composition, and reactor residence time via the mass flow rate per unit volume. The sensitivity of the chemical system to individual reaction rate constants and feed composition can also be evaluated for prescribed pressure, temperature or enthalpy, and residence time.

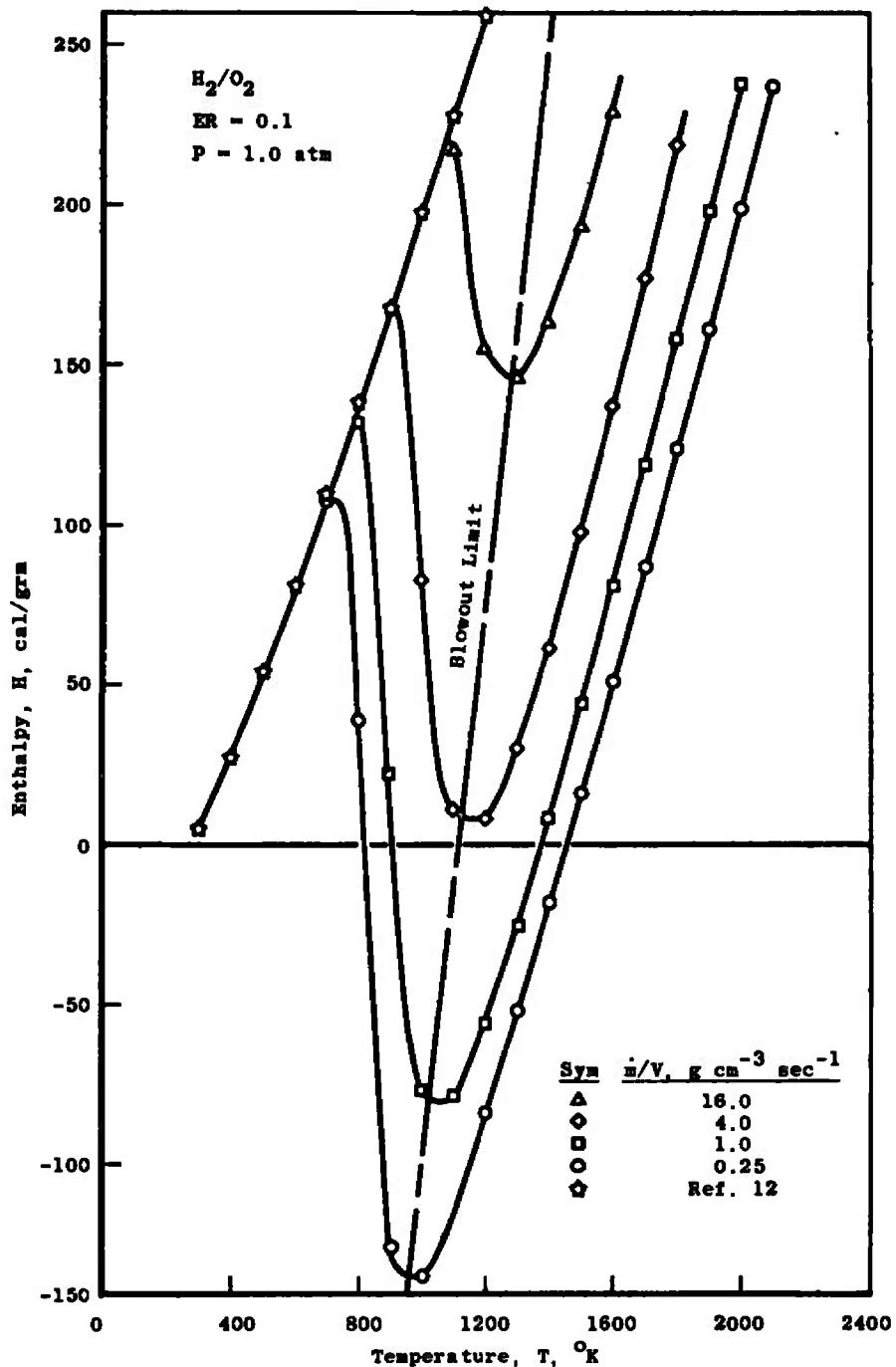
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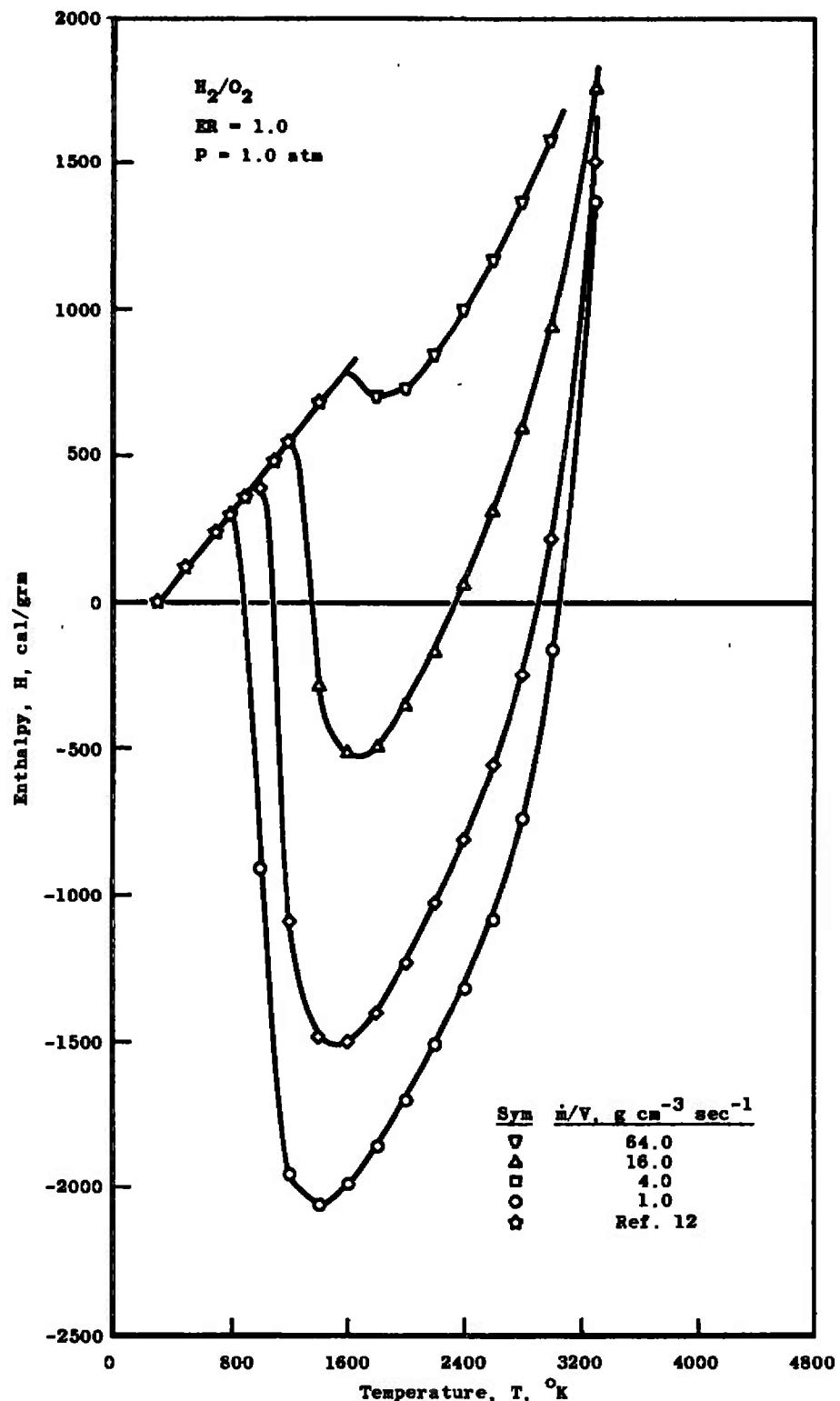
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APPENDIXES

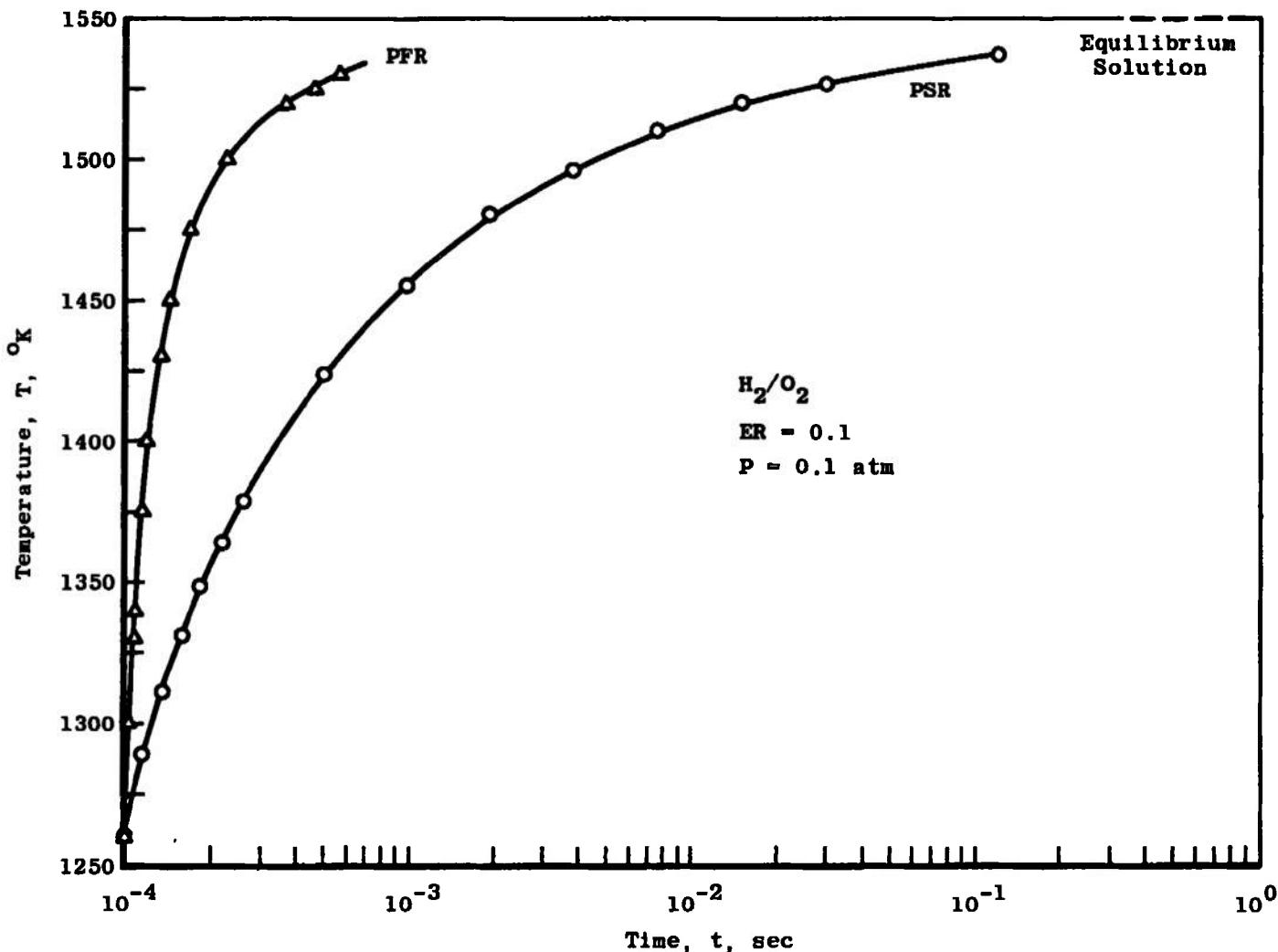
- I. ILLUSTRATIONS**
- II. TABLES**
- III. COMPUTER PROGRAM LISTING
AND SAMPLE OUTPUT**



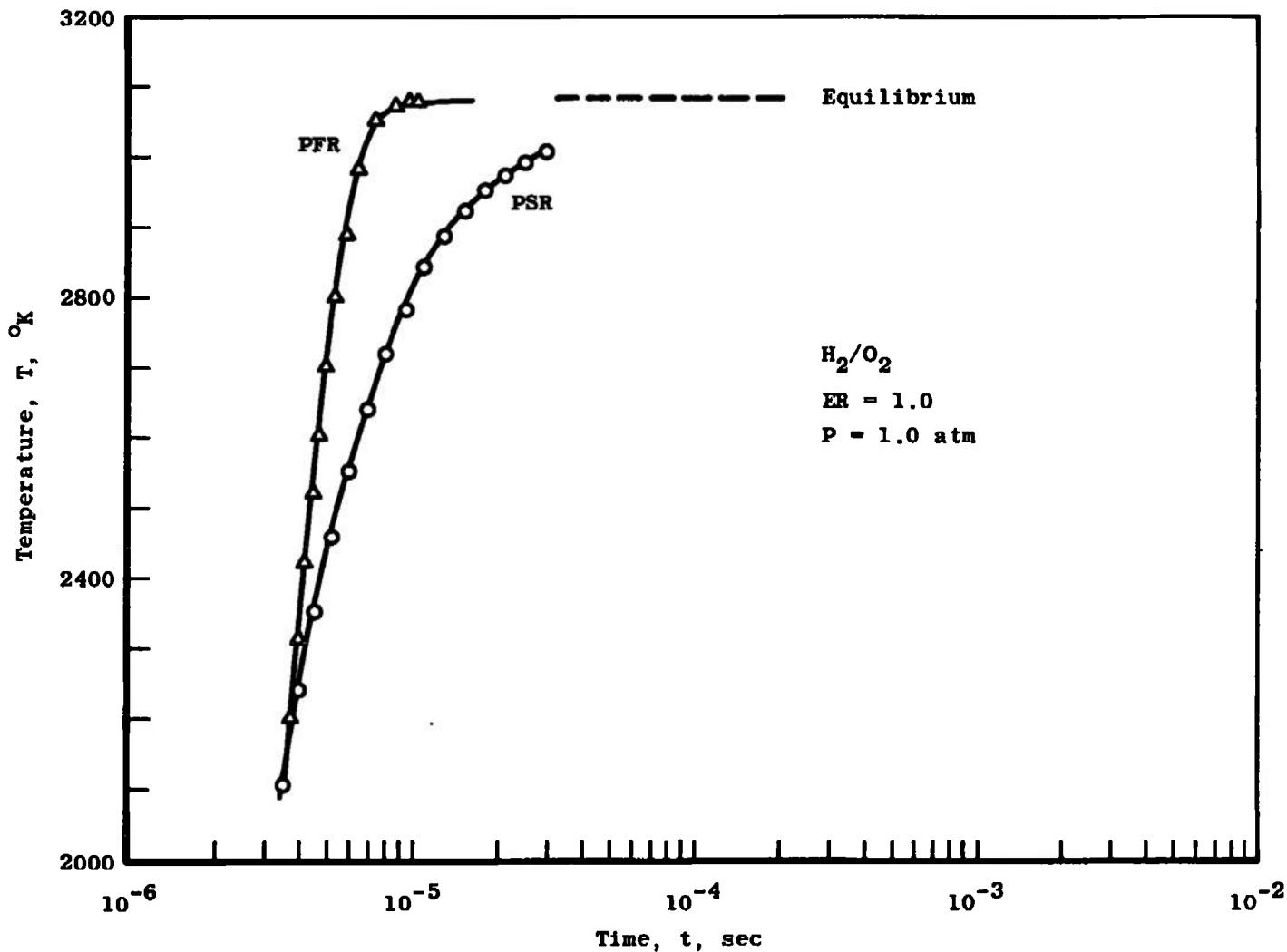
a. $ER = 0.1$
 Fig. 1 Enthalpy/Temperature Map for H_2/O_2



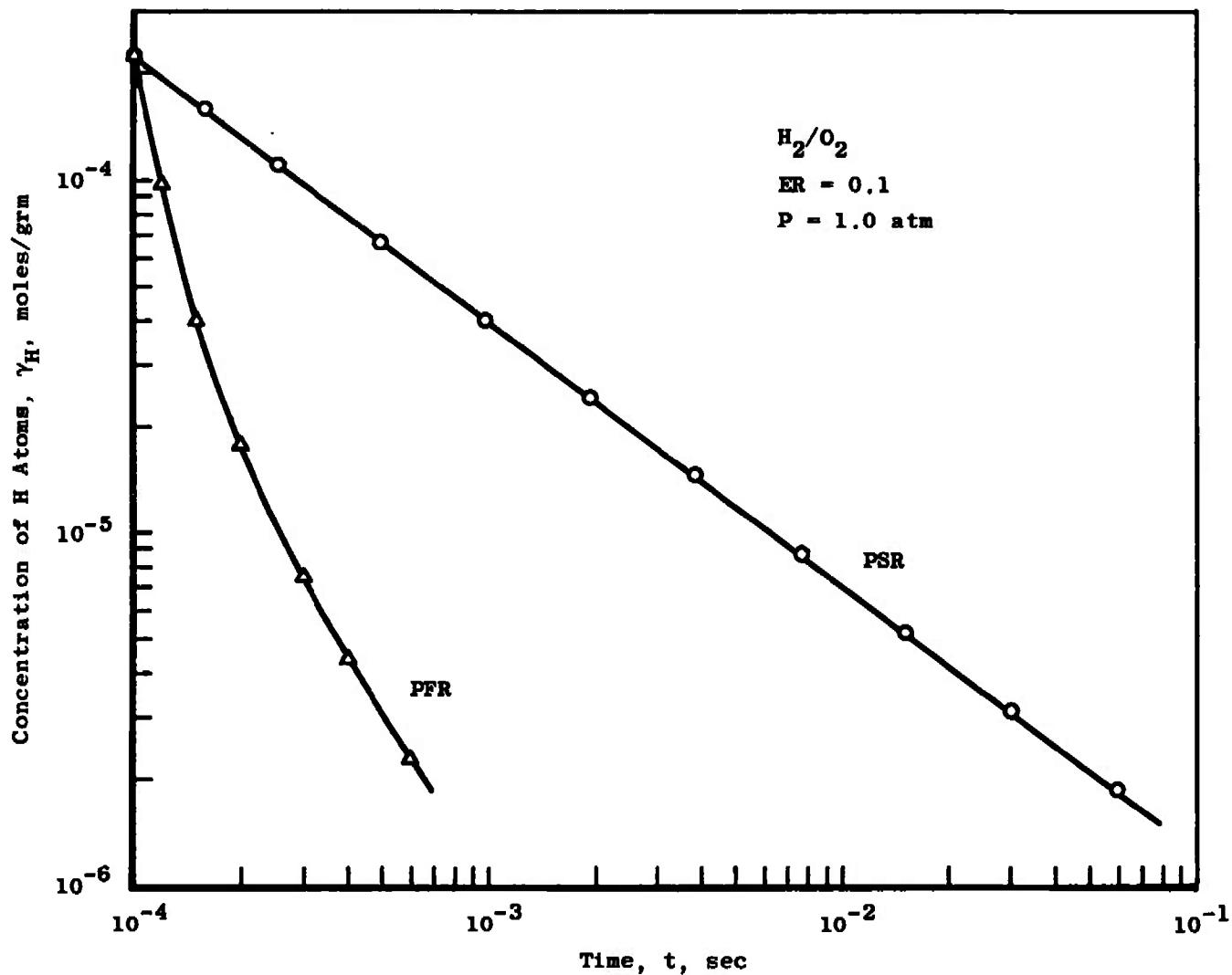
b. $ER = 1.0$
Fig. 1 Concluded



a. Temperature versus Time for H_2/O_2 , ER = 0.1, Enthalpy Constant
 Fig. 2 Comparison of Plug Flow Reactor and Perfect Stirred Reactor



b. Temperature versus Time for H_2/O_2 , $\text{ER} = 1.0$, Enthalpy Constant
Fig. 2 Continued



c. Concentration versus Time for H_2/O_2 , ER = 0.1, Enthalpy Constant
Fig. 2 Concluded

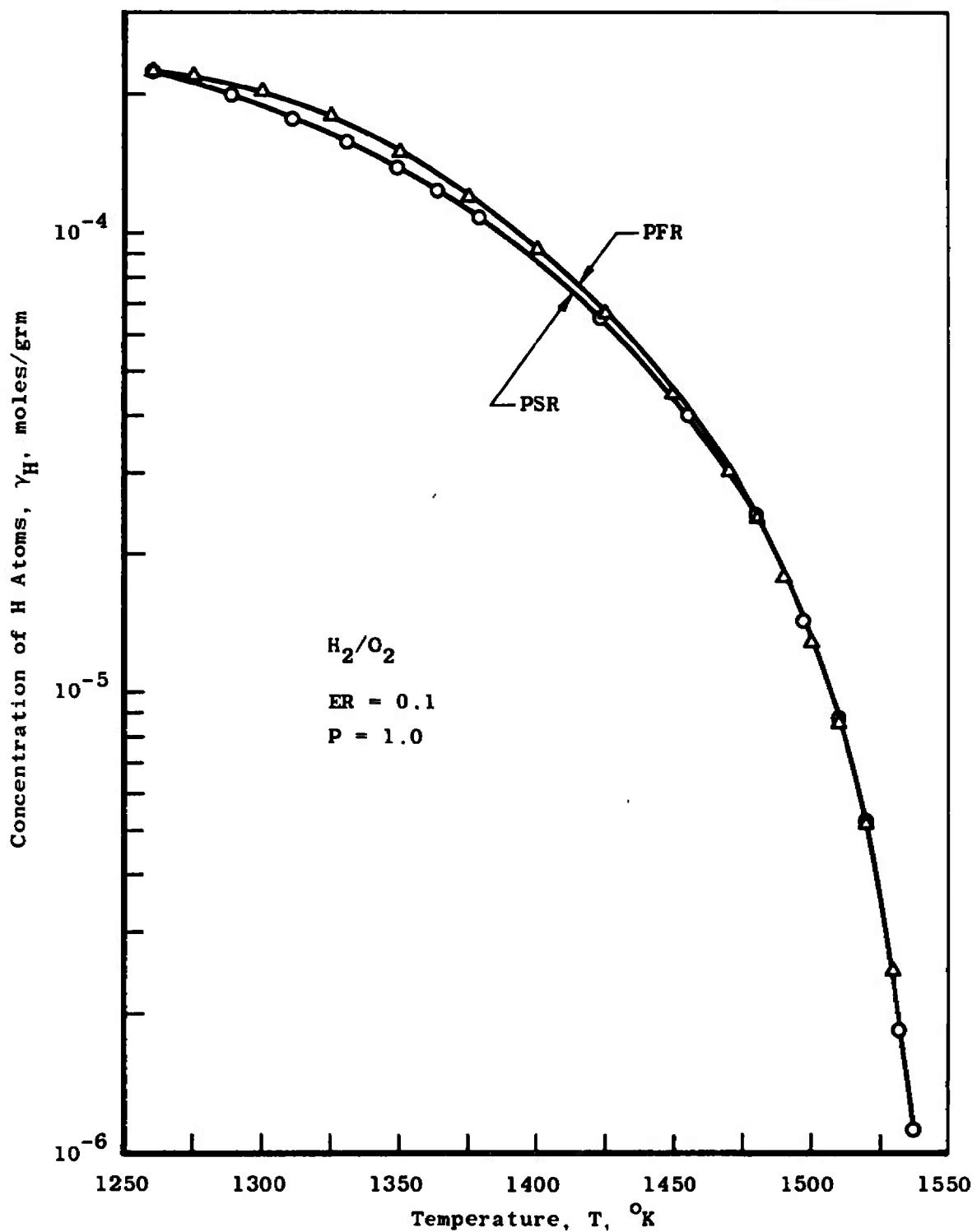


Fig. 3 Comparison of Plug Flow Reactor and Perfect Stirred Reactor:
 H Concentration versus Temperature for H_2/O_2 , ER = 0.1,
 Enthalpy Constant

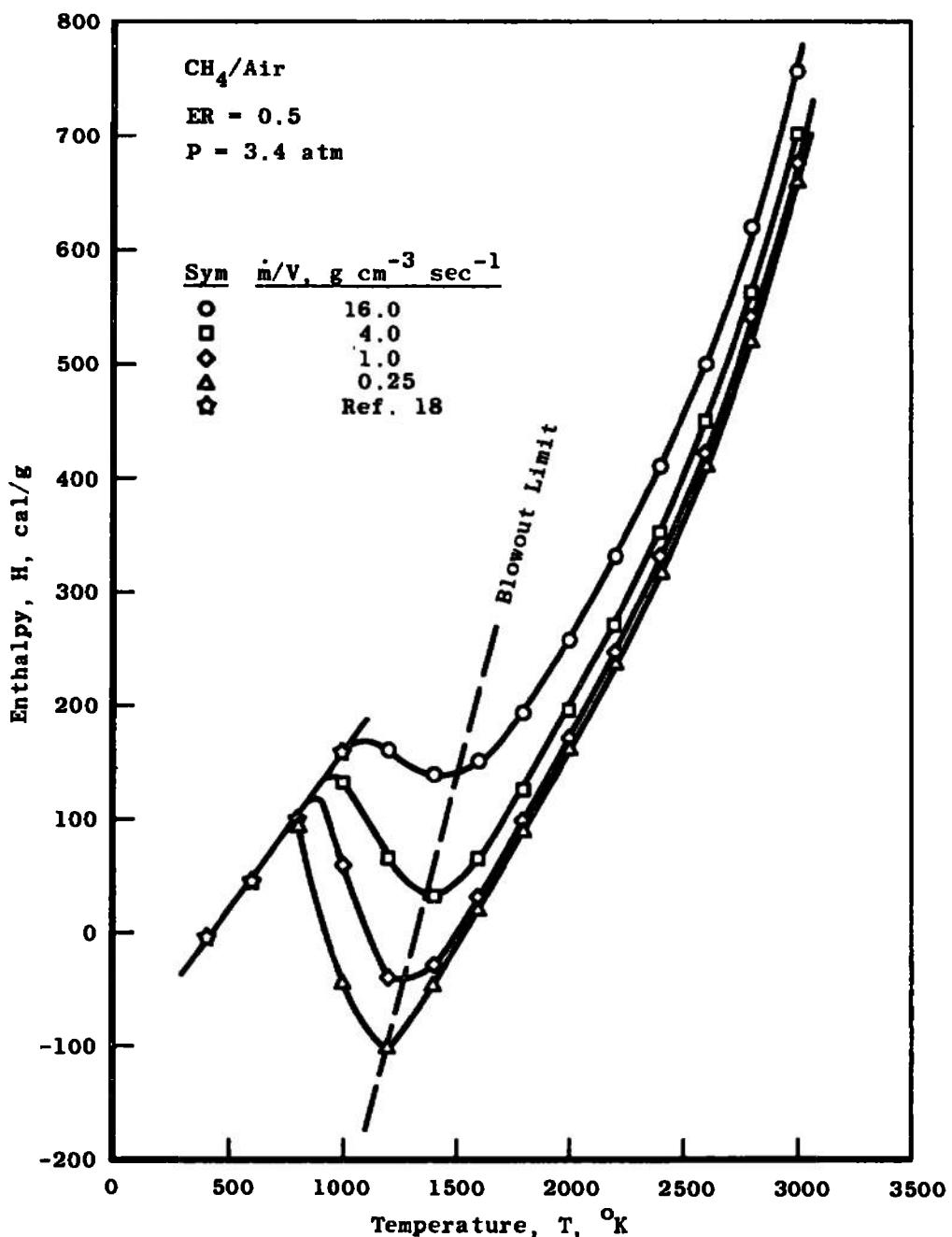


Fig. 4 Enthalpy/Temperature Map for CH₄/Air, ER = 0.5

TABLE I
HYDROGEN/AIR REACTION SET

$H_2 + O = H + OH$	$f = 2.25 \times 10^{12} e^{-3900/T}$
$H_2 + OH = H + H_2O$	$f = 2.20 \times 10^{14} e^{-5138/T}$
$O_2 + H = O + OH$	$f = 1.90 \times 10^{14} e^{-9007/T}$
$H_2O + O = OH + OH$	$f = 8.30 \times 10^{13} e^{-9108/T}$
$H + H + M = H_2 + M$	$f = 5.0 \times 10^{18} T^{-1.15}$
$O + O + M = O_2 + M$	$f = 4.7 \times 10^{15} T^{-2.28}$
$H + O + M = OH + M$	$f = 5.3 \times 10^{15} e^{1400/T}$
$H + OH + M = H_2O + M$	$f = 1.2 \times 10^{17} e^{252/T}$

Reaction scheme and rate data taken from Ref. 12

TABLE II
METHANE/AIR REACTION SET

$j = 1$	$\text{CH}_4 + \text{O} = \text{CH}_3 + \text{OH}$	$f = 1.7 \times 10^{13} e^{-4380/T}$
2	$\text{CH}_4 + \text{H} = \text{CH}_3 + \text{H}_2$	$f = 6.3 \times 10^{13} e^{-6350/T}$
3	$\text{CH}_4 + \text{OH} = \text{CH}_3 + \text{H}_2\text{O}$	$f = 2.8 \times 10^{13} e^{-2500/T}$
4	$\text{CH}_3 + \text{O}_2 = \text{CHO} + \text{H}_2\text{O}$	$f = 10^{11}$
5	$\text{CHO} + \text{OH} = \text{CO} + \text{H}_2\text{O}$	$f = 5.0 \times 10^{13}$
6	$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	$f = 3.1 \times 10^{11} e^{-300/T}$
7	$\text{O} + \text{H}_2 = \text{OH} + \text{H}$	$f = 3.0 \times 10^{13} e^{-4760/T}$
8	$\text{H} + \text{O}_2 = \text{OH} + \text{O}$	$f = 2.24 \times 10^{14} e^{844/T}$
9	$\text{O} + \text{H}_2\text{O} = \text{OH} + \text{OH}$	$f = 8.44 \times 10^{13} e^{9470/T}$
10	$\text{H}_2 + \text{OH} = \text{H} + \text{H}_2\text{O}$	$f = 2.19 \times 10^{13} e^{-2590/T}$
11	$\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$	$f = 2.0 \times 10^{19} \text{ T}^{-1}$
12	$\text{CHO} + \text{M} = \text{H} + \text{CO} + \text{M}$	$b = 1.0 \times 10^{13} e^{-14,400/T}$
13	$\text{CH}_4 + \text{M} = \text{CH}_3 + \text{H} + \text{M}$	$b = 1.5 \times 10^{19} e^{-50,300/T}$
14	$\text{N}_2 + \text{O}_2 = \text{NO} + \text{NO}$	$f = 1.36 \times 10^{14} e^{-37,750/T}$

Reaction scheme and rate data from Ref. 19 except for the last reaction whose rate constant is taken from Ref. 16 for the reaction $\text{O} + \text{N}_2 = \text{NO} + \text{NO}$.

TABLE III
SENSITIVITY COEFFICIENTS FOR THE METHANE/AIR SYSTEM

		$f_1 (\partial T / \partial f_1) ^\circ K$														
ER	m/V	T	$f_1 = 1$	2	3	4	5	6	7	8	9	10	11	12	13	14
0.5	1.0	2100	2.5	2.3	4.2	-5.7	10.3	13.9	2.2	2.3	2.5	2.2	9.9	-5.6	18.9	-1.8
		1900	1.0	0.8	2.8	-3.4	8.2	15.9	0.8	0.8	1.1	0.7	5.6	-6.5	12.7	-0.5
		1700	0.5	0*	3.2	0.9	5.2	21.3	0	0	0.8	0	2.2	-4.7	5.9	0
		1500	0.7	0	5.8	9.2	-2.0	36.0	0	1.4	2.2	0	0	2.2	-3.6	0
4.0	2100	1.2	1.1	6.4	15.0	8.8	34.8	0.8	1.0	1.7	0.7	1.8	-6.7	17.4	-0.6	
		1900	0.7	0.6	7.6	21.2	5.1	44.7	0	1.2	2.0	0	0.6	-4.4	6.6	0
		1700	2.0	0.7	12.0	34.3	-4.4	65.5	0.7	3.6	4.9	0	0	5.1	-9.7	0
		1500	10.6	8.7	36.2	103.1	-64.4	170.6	12.6	36.7	36.0	9.7	5.4	70.0	-68.0	-5.8
16.0	2100	1.8	1.3	16.0	81.1	3.3	58.9	0.7	2.9	4.4	0	0	-1.9	1.3	0	
		1900	2.4	1.7	22.4	94.6	-8.2	73.5	1.0	7.8	8.9	1.0	0.5	8.8	-18.2	0
		1700	7.1	5.4	45.3	149.6	-45.3	101.3	10.5	30.3	28.7	11.6	8.8	52.0	-57.8	-1.2
		1500	112.7	111.1	312.0	618.9	-244.4	266.8	202.9	351.1	250.7	221.7	208.0	471.3	-232.7	-12.2

* $f_j \frac{\partial T}{\partial f_j} < |0.5|$

APPENDIX III
COMPUTER PROGRAM LISTING AND SAMPLE OUTPUT

```

C
C      MAIN PROGRAM STIRRED REACTOR THEORY I.T.OSGERBY
      REAL MUDTV
      DIMENSION A(240)
      DIMENSION X0(20),X(20),W(20),B(20),B0(20),HM(20),Y(20),DCP(20),BD
      *(20),CPM(20),Y0(20)
      COMMON /SECOND/NN,N,N1,NR,NT,IT,M,L,N2,KOUNT,NT1
      COMMON/RGAS/RG,RR
      COMMON /EQL/F(20),DF(20)
      COMMON/FIFTH/NNT
      COMMON/HRCON/ICR,NR2,NR3,NR4
      C
      IT=1  TEMPERATURE CONSTANT
      ICR=80
      K=0
      JJ=2
100  CONTINUE
      READ(29,3) P,T,T0,DELT,IMIN
      IF(P.EQ.0.0) GO TO 101
      READ(29,2) MUDTV,DMUDV,N1,N,LT,MT,IT,NR, NN,NNT
      READ(29,1)(X0(I),I=1,NT)
      READ(29,1)(X(I),I=1,NT)
      READ(29,1)(W(I),I=1,NT)
C      COMPUTE SPECIES
      N1=N+1
      N2=N+2
      NT1=NT+1
      NX=N
      MY=N+1
20    RR=1.98/26
      RG=82.0567
      TT=T
      XX = 0.0
      YY=0.0
C      NORMALISE INPUTS
      DO 9 I=1,NT
      XX=XX+X(I)
      9 YY=YY+X0(I)
      DO 10 I=1,NT
      X(I)=X(I)/XX
      10 X0(I)=X0(I)/YY
      H0=0.0
      YY=0.0
      W0=0.0
      WM=0.0
      DO 4 I=1,NT
C      CALCULATE MOLEC. WT.
      W0=W0+X0(I)*W(I)
      WM=WM+X(I)*W(I)
      4 CONTINUE
      CALL BBS (T0,NT,HM,CPM,DCP,K)
C      CALCULATE FEED VALUES OF SPECIES AND ENTHALPY
      DO 30 I=1,NT
      B0(I)=X0(I)/W0
      H0=H0+WM(I)*B0(I)
      30 CONTINUE
C      CALCULATE FEED DENSITY
      RD=P*W0/(82.056/*T0)
      WRITE (21,35) T0,H0
      WRITE (21,102)
      IF (IT-1) 28,29,28

```

```

28 WRITE (21,31)
  GO TO 14
29 WRITE (21,32)
C  DEFINE MASS FLOW RATE / UNIT VOLUME
14 DO 12 L=1,LT
  IF (L.EQ.1) GO TO 13
  T=TT
  MDOTV=MDOTV*UDMV
13 DO 11 I=1,NT
C  CALCULATE INITIAL REACTOR SPECIES
11 B(I)=X(I)/WW
C  SET TEMPERATURE ESTIMATE
  DO 12 M=1,MT
  IF (M.EQ.1) GO TO 18
  T=T-DELT
  IF ((T-TMIN).LT.DELT) M=MT
18 CALL B33 (T,NT,HH,CPM,UCP,K)
C  CHECK FOR NON-CONVERGED SOLUTION OR BLOW OUT
  IF (KOUNT.EQ.60) GO TO 22
  DO 21 J=N1,N2
  Y0(J)=B(J)/B0(J)
  IF (ABS(Y0(J)-1.0).GT.0E-3) 22,22,23
21 CONTINUE
22 DO 15 I=1,NT
16 B(I)=X(I)/WW
C  ESTIMATE REACTOR DENSITY AND RESIDENCE TIME
23 R=R/(82.0567*T)*WW
  TAU=R/MDOTV
  CALL TIMER (TT1)
  CALL C9MP (B,B0,P,T,R,Y,H,H0,CP,TAU,WW,XX,BD,A,NX,MY)
  CALL TIMER (TT2)
  TIME=TT2-TT1
  WRITE(21,34) TIME
  WRITE(21,33) N,NT,II,NR,KOUNT,H,L,NX,MY,MT,LT
  WRITE(21,34) (B(I),B0(I),BD(I),Y(I),X(I),X0(I),I=1,NT)
  WRITE(21,7) P,T,R,RU,WW,H0,H,H0,CP
  WRITE(21,17) TAU,MDOTV
  JT=IT
  IF (VN) 43,15,43
43 CALL RCHECK (T,B,B0,P,R,Y,H,H0,CP,TAU,WW,BD,A,NX,MY,MDOTV,X0,H0,W)
  IT=JT
15 CONTINUE
12 CONTINUE
  GO TO 100
1  FORMAT(6E12.0)
2  FORMAT(2E10.0,6I5)
3  FORMAT(5E10.0)
7  FORMAT(9E12.4)
17 FORMAT(2E12.4//)
31 FORMAT (1H0,3X,19H ENTHALPY CONSTANT)
32 FORMAT (1H0,3X,22H TEMPERATURE CONSTANT)
33 FORMAT(1I15)
34 FORMAT (1E12.4)
35 FORMAT (3X,2E12.6)
39 FORMAT (3X,6E12.4)
102 FORMAT (1H1,3X,47H ADIABATIC WELL-STIRRED REACTOR CALCULATIONS)
101 STOP
  END
0000 ERRORS.  COMPILEATION COMPLETE.

```

```

SUBROUTINE COMP(B,B0,P,I,R,Y,H,H0,CP,TAU,WW,XX,BD,D,NX,MY)
DIMENSION B(20),B0(20),U(NX,MY),A(20,20),C(20),DBDB(20,20),DBDT(20),
*, DBDR(20), BD(20),HM(20),CPM(20),UCPT(20),DP(20),Y(20),Y0(20)
*,YS(20)
COMMON /SECOND/NN,N,N1,NR,NT,IT,IDUM(3),KOUNT,MDUM(1)
COMMON/RGAS/RG,RR
CA_L B31(A,C,B0)
KUNI=1
ICT=0
DE_T_=0.0
DO 6 K=1,60
KOUNT =K
C CALCULATE PARTIAL DERIVATIVES
CA_L B34(B,T,R,DBDB,DBDT,DBDR,BD)
C CALCULATE MATRIX COEF.
DO 1 J=1,N
DO 1 I=1,N
ZB=0.0
DO 2 L=N1,NT
ZB=ZB+(DBDB(J,L)-DBDR(J)*R*WW-BD(J)*WW)*A(I,L)
2 CONTINUE
D(J,I)=-TAU*(DBDB(J,I)-DBDR(J)*R*WW-BD(J)*WW+2B)
1 CONTINUE
DO 4 I=1,N
D(I,I)=1.0+U(I,I)
4 D(I,MY)=B0(I)-B(I)+TAU*BD(I)
C SOLVE MATRIX
CALL CHOLE (D,NX,MY,U)
28 IF(NX) 12,13,13
12 WRITE(21,14)
14 FORMAT(1H,3X,15HSINGULAR MATRIX)
NX=N
GO TO 100
13 DO 16 J=1,N
Y0(J)=B(J)
16 YS(J)=D(J,MY)
C TEST FOR CORRECTIONS TOO LARGE
ZPX=0.0
DO // J=1,N
ZPP=ABS(YS(J)/Y0(J))
IF (ZPP.GT.ZPX) ZPX=ZPP
7/7 CONTINUE
ZP=0.37/ZPX
IF (ZP.GT.1.0) ZP=1.0
C CORRECT SPECIES CONCENTRATIONS
DO 15 J=1,N
15 Y(J)=Y0(J)+YS(J)*ZP
DO 17 I=1,N
B(I)=Y(I)
17 Y(I)=(B(I)-BD(I))/(TAU* BD(I))-1.0
DO 18 J=N1,NT
Y0(J)=B(J)
B(J)=C(J)
BD(J)=0.0
Y(J)=0.0

```

```

JJ=J-1
DO 9 I=1,JJ
BD(J)=BD(J)+A(I,J)*BD(I)
9 B(J)=B(J)+A(I,J)*B(I)
IF (BD(J).EQ.0.0) GO TO 667
Y(J)=(Z(J)-BD(J))/(IAU*BD(J))-1.0
667 CONTINUE
IF (BD(J)) 37,38,37
37 Y0(J)=Z(J)/BD(J)
GO TO 39
38 Y0(J)=1.0
39 IF (Z(J)) 40,10,10
40 B(J)=1.0=-10
10 CONTINUE
WW=0.0
DO 18 I=1,NT
18 WW=WW+Z(I)
WW=1.0/WW
R0_U=R
R=P*WW/(RG+1)
TAU=TAJ*2/R0D
C ITERATION CONTROL
DO 32 J=N1,NT
IF (ABS(Y0(J)-1.0)-1.0E-4)32,32,7
32 CONTINUE
GO TO 20
7 IF (EP-1.0) 49,50,50
50 IF (IT-1) 52,49,52
52 CALL BBS(T,NT,HH,CPM,DCPT,KUNT)
H=0.0
CP=0.0
DO 53 I=1,NI
H=1+HM(I)*B(I)
53 CP=CP+CPM(I)*B(I)
C TIME PERIODURE CONTROL
IF (ICT-0) 54,55,54
55 DE_T=(H0-H)/CP
IF (DELT*DELT) 56,56,57
57 T=T+DELT*0.83
GO TO 54
56 T=T+DELT*0.38
54 ICT=1
ICT=ICT-1
DE_T=DELT
IF (T-200.0) 58,58,59
59 T=5000.0
GO TO 50
58 IF (T-500.0) 61,60,60
61 T=300.0
C TIME WITHIN 1 DEG K
60 IF (AHS(H0-H)-CP) 49,49,6
C CH=LK P.S.R. EQUATION
49 DO 8 I=1,N
IF (ABS(Y(I)) -5.0E-3) 8,8,6
8 CONTINUE

```

```

      GO TO 20
6  CONTINUE
20 IF(KOUNT.EQ.60) WRITE(21,99)
  XX=U.0
  H=0.0
  CP=U.0
  CALL BB3(T,NT,HM,CPM,DCPT,KUNT)
  DO 3 I=1,NT
  XX=XX+B(I)*WH
  H=H+HM(I)*B(I)
  3 CP=CP+CPM(I)*B(I)
100 RETURN
99 FORMAT(27H NO CONVERGENCE IN 60 STEPS)
  END
0000 ERRORS.  COMPIRATION COMPLETE.

```

```

SUBROUTINE BB1 (A,C,B)
DIMENSION A(20,20),B(20),C(20)
DIMENSION NS(20,5),SC(20,5),J(5)
COMMON/SECOND/NN,N,N1,NR,NT,NDUM(6)
DATA KTP/0/
IF (KTP) 3,3,4
3 NL=NT-N
  READ (29,98) (J(I),I=1,NL)
  DO 1 I=1,NL
  JJ=J(I)
  READ (29,99) (NS(K,I),SC(K,I) ,K=1,JJ)
  1 WRITE(21,999)(NS(K,I),SC(K,I) ,K=1,JJ)
999 FORMAT (5(I10,E12.4))
4 DO 6 I=1,20
  C(I)=0.
  DO 6 K=1,20
6 A(I,K)=0.
  DO 5 I=1,NL
  II=N+I
  C(II)=0.
  JJ=J(I)
  DO 2 K=1,JJ
  L=NS(K,I)
  C(II)=C(II)+B(L)*SC(K,I)
  A(L,II)=-SC(K,I)
2 A(II,II)=0.0
5 CONTINUE
99 FORMAT ( 8(I5, F5.0))
98 FORMAT (5I5)
  KTP=1
  RETURN
  END
0000 ERRORS.  COMPIRATION COMPLETE.

```

```

SUBROUTINE BB3(T,NT,HMI,CPMI,DCPTMI,K)
DIMENSION HMI(1),CPMI(1),DCPTMI(1)
DIMENSION COE(14),C(14,20)
DIMENSION CC(6),TT(5)
COMMON /EOL/F(20),DF(20)
RG=1.98/26
TT_N = ALOG(T)
TLN = 1.-TTLN
IF (K) 4,7,4
7 WRITE (21,103)
103 FORMAT (1H1,3X,34H THERMO DATA CHECK DATA AT T0)
      REAU (29,70)((C(I,KK),I=1,14),KK=1,NT)
/0 FORMAT(/E11.0)
4 TE=T
IF (TE-300.)10,20,2U
10 WRITE(21,80) T
80 FORMAT (54H0 TEMPERATURE IS OUT OF RANGE OF CURVE FIT TABLES, T =,
11PE12.5)
CALL EXIT
20 IF (TE-1000.)30,40,40
30 KL=0
GO TO 60
40 IF (TE-5000.) 50,50,10
50 KL=/
60 CONTINUE
TT(1)=T
DO 1 M=2,4
1 TT(M)= TT(M-1)*T
TT(5)=1./T
DO 100 KK=1,NT
DO 5 J=1,14
5 COE(J)=C(J,KK)
CC(1)= COE(KL+1)
DO 3 J=2,6
KKK=(KL+J)
3 CC(J)= COE(KKK)*TT(J-1)
H=          CC(1)+.5*CC(2)+CC(3)/3.+.25*CC(4)+.2*CC(5)+CC(6)
FX = (CC(1)*TLN )-.5*CC(2)-(CC(3)+.5*CC(4))/6.-.05*CC(5)+CC(6)-
*COE(KL+1)
CP =          (CC(1)+CC(2)+CC(3)+CC(4)+CC(5))
DCP=CC(2)+2.*CC(3)+3.*CC(4)+4.*CC(5)
C SPECIES ENTHALPY
HMI(K)=H*RG*T
C SPECIES HEAT CAPACITY
CPMI(K)=CP*RG
C SPECIES HEAT CAPACITY DERIVATIVE
DCPTMI(KK)=DCP*RG/T
C SPECIES FREE ENERGY
F(KK)=FX
C SPECIES FREE ENERGY DERIVATIVE
DF(KK)=-H/T
IF (K.EQ.0) WRITE (21,/1) HMI(KK),CPMI(KK),F(KK),DF(KK)
/1 FORMAT (1H0,1P4E15.5/)
100 CONTINUE
K=1
RETURN
END
0000 ERRORS.  COMPILEATION COMPLETE.

```

```

SUBROUTINE CHOLESS(A,N,M,MATSYM)
DIMENSION A(N,M)
IF(A(1,1).NE.0.0) GO TO 47
DO 37 J=2,N
IF(A(J,1).EQ.0.0) GO TO 37
IF(IIP=J
GO TO 27
37 CONTINUE
GO TO 54321
27 DO 57 K=1,M
TEMP=A(IFLIP,K)
A(IFLIP,K)=A(1,K)
A(1,K)=TEMP
57 CONTINUE
47 DO 27 J=2,M
A(1,J)=A(1,J)/A(1,1)
27 CONTINUE
DO 6 I=2,N
DO 7 J=2,M
IF(MATSYM.EQ.0)GO TO 49
IF(I-J)69,69,67
49 IF(J.GT.I)GO TO 69
68 K=J-1
SUM=0.0
DO 5 IR=1,K
SUM=SUM+A(I,IR)*A(IR,J)
5 CONTINUE
A(I,J)=A(I,J)-SUM
GO TO 7
69 K=I-1
SUM=0.0
DO 4 IR=1,K
SUM=SUM+A(I,IR)*A(IR,J)
4 CONTINUE
IF(A(I,I).EQ.0.0) GO TO 54321
A(I,J)=(A(I,J)-SUM)/A(I,I)
GO TO 7
67 A(I,J)=A(J,I)*A(J,J)
7 CONTINUE
6 CONTINUE
DO 52 L=2,N
I=L+1-K
SUM=0.0
LL=L+1
DO 51 IR=LL,N
SUM=SUM+A(I,IR)*A(IR,M)
51 CONTINUE
A(I,M)=A(I,M)-SUM
52 CONTINUE
GO TO 12345
54321 N=-1
12345 RETURN
END
0000 ERRORS.  COMPILEATION COMPLETE.

```

```

SUBROUTINE B34 (B,T,R,DBDB,DBDT,DBDR,BD)
DIMENSION DBDB(20,20),BD(20),DBDT(20),DBDR(20),B(20)
COMMON/SECOND/NN,N,N1,NR,NT,IT,1DUM(3),KOUNT,NT1
COMMON/RATE/TT,FF(80),BB(80),DFF(80),DBB(80)
DIMENSION D(80,18),I1(80,7),ER(80,7),KS(80,7),IE(80),IC(80)
COMMON /RRATE/A(80),EX(80),TEX(80),KK(80,4),ITR(80),ITP(80),
*IB(HU)
DATA KRD/0/
IF (KRD) 1,1,2
C      NT1      TEMP
C      NT2      DENSITY
C      NT3      X
1  NT1=NT+1
NT2=NT+2
NT3=NT+3
KRD=1
B(NT1)=1.
READ (29,99) NR
DO 10 IR=1,NR
WRITE (21,97) IR
READ (29,99) ITR(IR),ITP(IR),(KK(IR,I),I=1,4),A(IR),EX(IR),
*TEX(IR),IE(IR),IC(IR),IB(IR)
WRITE (21,999) (KK(IR,I),I=1,4),A(IR),EX(IR),TEX(IR),IE(IR),
*IC(IR),IB(IR)
999 FORMAT (4I10,3E14.6,4I5)
12 IF (IE(IR)) 11,11,14
14 L=IE(IR)
READ (29,96) (I1(IR,I),ER(IR,I),I=1,L)
WRITE (21,997) (I1(IR,I),ER(IR,I),I=1,L)
997 FORMAT (5(I10,E12.4))
11 DO 16 I=1,4
16 KS(IR,I)=KK(IR,I)
IF (IC(IR)) 10,10,1/
17 M=IC(IR)
READ (29,97) (KS(IR,I),I=1,M)
WRITE (21,97) (KS(IR,I),I=1,M)
10 CONTINUE
2 CONTINUE
TT=T
BS=0.
DO 18 I=1,NT
18 BS=BS+B(I)
IF (KOUNT.GT.1.AND.IT.EQ.1) GO TO 888
CALL RATES
888 CONTINUE
DO 100 IR=1,NR
DO 19 I=1,NT
19 D(IR,I)=0.
K1=KK(IR,1)
K2=KK(IR,2)
K3=KK(IR,3)
K4=KK(IR,4)
IF (ITP(IR)-ITR(IR)) 30,20,20
20 IF (ITR(IR)-1) 60,60,21
C      EVALUATE THIRD BODY EFFICIENCIES

```

```

60  CONTINUE
  BSJM=BS
  IF (IE(IR)) 61,61,62
62  K=IE(IR)
  DO 63 J=1,K
  JJJ=I1(IR,J)
63  BSJM=BSUM+ER(IR,J)*B(JJJ)
61  D1=FF(IR)*B(K1)
  D2=-BB(IR)*B(K2)
  U(IR,K1)=FF(IR)*BSUM
  U(IR,K2)=-BB(IR)*BSUM
  DO 64 J=1,N1
64  D(IR,J)=U(IR,J)+D1+D2
  IF (IE(IR)) 65,65,66
66  DO 67 J=1,K
  JJJ=I1(IR,J)
67  J(IR,JJJ)=D(IR,JJJ)+(D1+D2)*ER(IR,J)
65  D(IR,NT1)=(D1+D2)*BSUM
  D(IR,NT2)=(UFF(IR)*D1+DBB(IR)*D2)*BSUM
  D(IR,NT3)=U(IR,NT1)
  GO TO 100
C   EVALUATE TYPE  A+B=C+U
21  CONTINUE
  D(IR,K1)=FF(IR)*B(K1)
  D1=U(IR,K1)*B(K1)
  D(IR,K2)=FF(IR)*B(K1)+D(IR,K2)
  U(IR,K3)=-BB(IR)*B(K4)
  D2=U(IR,K3)*B(K3)
  D(IR,K4)=-BB(IR)*B(K3)+D(IR,K4)
  J(IR,NT1)=D1+D2
  D(IR,NT2)=D1*UFF(IR)+D2*DBB(IR)
  D(IR,NT3)=D(IR,NT1)
  GO TO 100
C   EVALUATE TYPE  A+A+M=A2+M
30  BSJM=BS
  IF (IE(IR)) 311,311,31
31  K=IE(IR)
  DO 32 J=1,K
  LL=I1(IR,J)
35  BSJM=BSUM+ER(IR,J)*B(LL)
311 D1=FF(IR)*B(K1)*B(K2)*R
  D2=-BB(IR)*B(K3)
  U(IR,K1)=FF(IR)*B(K2)*BSUM*R
  U(IR,K2)=FF(IR)*B(K1)*BSUM*R +D(IR,K2)
  D(IR,K3)=-BB(IR)*BSUM
  DO 32 J=1,NT
32  D(IR,J)=D(IR,J)+D1+D2
  IF (IE(IR)) 36,36,34
34  DO 35 J=1,K
  LL=I1(IR,J)
33  D(IR,LL)=D(IR,LL)+(D1+D2)*ER(IR,J)
36  D(IR,NT1)=(D1+D2)*BSUM
  D(IR,NT2)=(D1*UFF(IR)+D2*DBB(IR))*BSUM
  D(IR,NT3)=(2.*D1+D2)*BSUM
100  CONTINUE

```

```
C      CALCULATE PARTIAL DERIVATIVES
      DO 40 J=1,NT3
      DO 40 I=1,N
40  D8D8(I,J)=0.
      DO 50 IR=1,NR
      K=ITR(IR)
      L=ITP(IR)+K
      M=K+1
      DO 50 J=1,NT3
      DO 51 I=1,K
      LL=KS(IR,I)
51  D8D8(LL,J)=DBDB(LL,J)-D(IR,J)
      DO 52 I=M,L
      LL=KS(IR,I)
52  D8D8(LL,J)=DBDB(LL,J)+D(IR,J)
50  CONTINUE
      DO 72 K=1,N
      DO 71 J=1,NT
71  D8D8(K,J)=D8D8(K,J)*R
      BD(K)=DBDB(K,NT1) *R
      DBDT(K)=DBDB(K,NT2) *R
      DBDR(K)=DBDB(K,NT3)
72  CONTINUE
99  FORMAT (6I5,3E10.0,3I5)
98  FORMAT (5(I5,E10.0))
97  FORMAT (10I5)
      RETURN
      END
0000 ERRORS.  COMPILED COMPLETE.
```

```

SUBROUTINE RATES
COMMON/RATE/ T,FR(80),BR(80),DFR(80),DBR(80)
COMMON/RGAS/RR,R
COMMON /EQL/F(20),DF(20)
COMMON /RRATE/A(80), E(80),TEX(80),KK(80,4),ITR(80),ITP(80),
*IB(80)
COMMON/SECOND/NN,N,N1,NR,NT,IDUM(5),NT1
COMMON/RRCON/ICR,NR2,NR3,NR4
RT=1./T
RTT= RT/T
RRT=1./(RR+T)
DRRT=-1./T
F(NT1)=0.
DF(NT1)=0.
IF (NN) 6,7,6
6 A(ICR)=1.001*A(ICR)
7 DO 100 IR=1, NR
DBR(IR)=0.
BR(IR)=0.
DFR(IR)=0.
FR(IR)=A (IR)
IF (E(IR)) 1,2,1
1 FR(IR)=FR(IR)*EXP(-E(IR)*RT)
DFR(IR)=E(IR)*RTT
2 IF (TEX(IR)) 3,4,3
3 FR(IR)=FR(IR)*T*TEX(IR)
DFR(IR)=DFR(IR)+TEX(IR)/T
4 IF (IB(IR)) 5,100,5
5 K=KK(IR,1)
L=KK(IR,2)
J=KK(IR,3)
I=KK(IR,4)
EQ=F(I)+F(J)-F(K)-F(L)
IF (EQ+70.) 100,9,9
9 DEQ=DF(I)+DF(J)-DF(K)-DF(L)
EQ=EXP(EQ)
IF (IB(IR)) 11,100,10
10 BR(IR)=FR(IR)*EQ
DBR(IR)=DFR(IR)+DEQ
IF (ITP(IR)-ITR(IR)) 8,100,100
8 BR(IR)=BR(IR)*RRT
DBR(IR)=DBR(IR)+DRRT
GO TO 100
11 B=FR(IR)/(EQ+RRT)
DB=DFR(IR)-DEQ-DRRT
BR(IR)=FR(IR)
DFR(IR)=DFR(IR)
FR(IR)=B
100 CONTINUE
IF (NN) 12,13,12
12 A(ICR)=A(ICR)/1.001
13 RETURN
END
0000 ERRORS. COMPILEATION COMPLETE.

```

```

SUBROUTINE RCHEK (TT,B,HO,P,R,Y,H,HO,CP,TAU,WW,     BD,A,NX,MY,MDOTV
*,X0,HO,W)
REAL MDOTV
DIMENSION A (240)
DIMENSION X0(20),          W(20),B(20),BU(20),HM(20),Y(20),DCP(20),BD
*(20),CPM(20),Y0(20),DLEI(80),BSAV(20),Z0(20),D0(20)
COMMON /SECOND/NN,N,N1,NR,NT,IT,M,L,N2,KOUNT,NT1
COMMON /FIFTH/NNT
COMMON /RGAS/RG,RR
COMMON /RRCON/ICR,NR2,NRS,NR4
K=1
NR4=NR+1
DO 20 I=1,NT1
Z0(I)=X0(I)
D0(I)=Z0(I)
20 CONTINUE
Z0(NT1)=Z0(5)
DO 98 IMR=1,NNT
CALL TIMER (TT1)
IF (IMR-1) 1,2,1
C INCREASE SPECIES NN
1 Z0(NN)=Z0(NN)+0.005*Z0(NT1)
WT4=0.0
DO 3 I=1,NT
Z0(I)=Z0(I)/(1.0+Z0(NN))
WT4=WT4+Z0(I)*W(I)
3 CONTINUE
DO 4 I=1,NT
D0(I)=Z0(I)/WT4
4 CONTINUE
2 T=TT
CALL B33 (T,NT,HH,CPM,DCP,K)
IT=1
R=P/(82.0567*T)*WW
TAU=R/MDOTV
ICR=80
C CALCULATE FEED ENTHALPY
CALL C3MP (B,D0,P,T,R,Y,H,HO,CP,TAU,WW,XX,BD,A,NX,MY)
IF (KOUNT.EQ.60) GO TO 39
DO 19 I=1,NT
BSAV(I)=B(I)
19 CONTINUE
IT=2
HO=H
C CALCULATE SENSITIVITY COEF. FOR EACH REACTION
DO 5 ICR=1,NR4
IF (KOUNT.EQ.60) GO TO 6
DO 7 J=N1,N2
Y0(J)=B(J)/D0(J)
IF (ABS(Y0(J)-1.0)>.0E-3) 7,/,8
7 CONTINUE
6 DO 9 I=1,NT
9 B(I)=BSAV(I)
8 R=P/(82.0567*T)*WW
TAU=R/MDOTV

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CALL CSMP (B,DO,P,T,R,Y,H,H0,CP,TAU,WW,XX,BD,A,NX,MY)
DLET(ICR)=T
IF (KOUNT.EQ.60) GO TO 59
DO 40 I=1,NT
BSAV(I)=9(I)
40 CONTINUE
5 CONTINUE
59 CONTINUE
CALL TIMER (TT2)
TIME=TT2-TT1
IF (IT-1) 29,29,28
28 WRITE (21,31)
GO TO 53
29 WRITE (21,32)
33 WRITE(21,11) TIME
DO 16 ICR=1,NR4
16 DLET(ICR)=(DLET(ICR)-DLET(NR4))*1000.0
C SENSITIVITY COEF. IS DLET
WRITE(21,12) (DLET(ICR),ICR=1,NR4)
WRITE(21,13) N,NT,IT,NR,KOUNT,M,L,NX,MY,IMR
WRITE (21,14) (B(I),DO(I),BD(I),Y(I),I=1,NT)
WRITE(21,12)P,T,R,RU,WW,WTM,H,H0,CP
WRITE(21,15) TAU,MDOTV
98 CONTINUE
RETURN
1J FORMAT (1H0,3X,19H ENTHALPY CONSTANT)
11 FORMAT (1E12.4//).
12 FORMAT(9E12.4)
13 FORMAT(915)
14 FORMAT (3X,4E14.6)
15 FORMAT(2E12.4///)
31 FORMAT (1H0,3X,19H ENTHALPY CONSTANT)
32 FORMAT (1H0,3X,22H TEMPERATURE CONSTANT)
END
0000 ERRORS. COMPILED COMPLETE.

```

DATA CARDS

Initial Conditions

P	R	TO	DEL F	TMIN					
.440301	.213004	.300003	.200003	.500005					
MIKOTV	DMDY	NT	N	LT	MT	IT	NR	NN	NNT
.1000001	.2000000	13	9	1	1	1	14	0	0
X(XI)	X(I)			W(I)					
.300330070000	.268190000-04			.100000000+01					
.100000030000	.111100000-03			.160000000+02					
.300300030000	.275000000-05			.170000000+02					
.000300000000	.329600000-02			.180160000+02					
.142800030002	.411000000-05			.160420000+02					
.000900000000	.150000000-04			.150340000+02					
.900030000000	.102800000-06			.290160000+02					
.000030000000	.187400000-03			.280100000+02					
.000003000000	.172200000-03			.300080000+02					
.000000300000	.155500000-02			.440100000+02					
.000000030000	.497400000-04			.201600000+01					
.515202700-02	.348000000-02			.320000000+02					
.19434700-01	.265400000-01			.280160000+02					

TH=N=0 DATA	Coefficients:							
.290000000+01	.000000000+00	.000000000+00	.000000000+00	.000000030+01	.25470497+05	.46001076+00	300<T<1000	
.220000000+01	.000000000+00	.000000000+00	.000000000+00	.000000000+00	.25470497+05	.46001076+00	1000<T<5000	
.3021984+01	.-21737250-02	.37342203-05	.-29947200-05	.90777990-12	.29137190+05	.244601076+01		
.303723567+01	.-18422190-04	.-88017920-08	.59643620-11	.-55743600-15	.29230007+05	.494679-2+01		
.30234708+01	.-11187230-02	.1246619+03	.-21035990-09	.-25246500-13	.35552787+04	.58253029+00		
.28893544+01	.-99835061-03	.-21979900-06	.19802780-10	.-38452900-15	.38811792+04	.55597016+01		
.41365016+01	.-17244500-02	.56982420-03	.45930000-08	.-14233650-11	.-30208800+05	.688162+0+0		
.H2O	.2670753+01	.30317120+02	.-85351000+06	.-11796850-09	.-61973600-14	.-29891000+05	.688131+1+01	
.4447678+01	.-69126000-02	.31602180-04	.29715400-07	.95103500-11	.-10166432+05	.-9175491+0-1		
.CH4	.11795744+01	.10950590-01	.-40221100-05	.71370200-09	.-4490000-13	.-95556627+04	.1250194-02	
.33995052+01	.42678350-02	.-20326800-06	.-11548030-05	.41268400-12	.-15649793+05	.27037468+01		
.CH3	.28927632+01	.62904500-02	.-22891900-05	.38993100-09	.-29276000-13	.-15787492+05	.568411+0+01	
.CHO	.38647156+01	.-53708660-03	.69345000-05	.-66450000-00	.-20577000-11	.-27795993+04	.48971857+01	
.32708241+01	.35195800-02	.-13772900-05	.243140-09	.-16727000-13	.-27820147+04	.73044232+01		
.CO	.3/371332+01	.-21709000-02	.50757340+05	.-34737700-05	.77216800-12	.-14363200+05	.263354+9+01	
.2951119+01	.15525770-02	.-61911400-06	.11350300-09	.-77883000-14	.-14231827+05	.65314450+01		
.NO	.4146947+01	.-41197230-02	.96922467+05	.-70633640-08	.22309510-11	.97447894+04	.25694290+01	
.3152936+01	.14059455-02	.-57378460-06	.10928820-09	.-73720800-14	.-98522040+04	.6944665+01		
.CO2	.21701000+01	.10378120-01	.-10733900-04	.65459180-05	.-16281000-11	.-48352602+05	.10664358+02	
.44129956+03	.31922960-02	.-12978200-05	.24147400-09	.-16743000-13	.-48944043+05	.728737+0+0		
.H2	.2846158+01	.41937120-02	.-98119300-05	.95122660-08	.-33093400-11	.-98725400+03	.-14117850+01	
.30445897+01	.61187110-03	.-73993500-08	.-20331900-10	.-24593798-14	.-85491000+03	.-164835+01		
.37185946+01	.-25167290-02	.85937353-05	.-82998720-08	.-77082100-11	.-10576700+04	.3900174+01		
.O2	.33975129+01	.78145603-03	.-22356670-06	.42490150-10	.-33460200-14	.-11927910+04	.374926+9+01	
.N2	.36315148+01	.-13332800-02	.26504100-05	.-97688310-09	.-99772200-13	.-10628300+04	.226749+0+01	
.28445761+01	.15976320-02	.-62566200-06	.11315850-09	.-76897100-14	.-89017445+03	.639017+0+01		

	THERMO DATA	CHECK DATA	AT	TO	h_i/RT^2
	h_i	C_{p_i}		R_i/RT	
H	5.21069+04	4.96815+00		7.36022+01	-2.91339-01
O	5.95663+04	5.23444+00		8.05398+01	-3.33046-01
OH	9.32571+03	7.14211+00		-6.46677+00	-5.21416-02
H ₂ O	-7.77831+04	8.02760+00		-1.19645+02	3.23075-01
CH ₄	-1.78732+04	8.53504+00		-5.24020+01	9.99323-02
CH ₃	3.35080+04	9.28114+00		3.28309+01	-1.87349-01
CHO	-3.15905+03	8.27126+00		-3.23501+01	1.77187-02
CO	-2.64028+04	6.96560+00		-6.80667+01	1.47623-01
NO	2.16132+04	7.13246+00		1.08962+01	-1.20843-01
CO ₂	-9.40354+04	8.89425+00		-1.83457+02	5.25768-01
H ₂	1.27436+01	6.89381+00		-1.57046+01	-7.12515-05
O ₂	1.29930+01	7.02368+00		-2.46606+01	-7.26461-05
N ₂	1.28851+01	6.96133+00		-2.30323+01	-7.20428-05
		TO			
		HO			
	.500000+03	-.311001+02			

BB1 DATA CARDS

5	7	8	2	6	.1000+01	7	.1000+01	8	.1000+01	10	.1000+01
5	.1000+01	4	.1000+01	5	.2000+01	6	.1500+01	1	.5000+00		
3	.5000+00	7	.5000+00								
12	.1000+01	10	.1000+01	7	.5000+00	2	.9000+00	3	.5000+00		
4	.5000+00	8	.5000+00	9	.5000+00						
13	.1000+01	9	.5000+00								

BB4 DATA CARDS

IR	1	KK(IR,J)		A(IR)	EX(IR)	TEX(IR)	IE(IR)	IC(IR)	IB(IR)	
1	5	2	6	3	.170000+14	.438000+04	.000000+00	0	0	1
2	5	1	6	11	.630000+14	.635000+04	.000000+00	0	0	1
3	5	3	6	4	.280000+14	.250000+04	.000000+00	0	0	1
4	6	12	7	4	.100000+12	.300000+00	.000000+00	0	0	1
5	7	3	8	4	.500000+14	.300000+00	.000000+00	0	0	1
6	3	8	10	1	.310000+12	.300000+03	.000000+00	0	0	1
7	11	2	3	1	.300000+14	.476000+04	.000000+00	0	0	1
8	12	1	2	3	.224000+15	.844000+04	.000000+00	0	0	1
9	4	2	3	3	.844000+14	.947000+04	.000000+00	0	0	1
10	11	3	1	4	.219000+14	.259000+04	.000000+00	0	0	1
11	3	1	4	14	.200000+20	.000000+00	-.100000+01	0	0	1
12	1	8	7	14	.200000+14	.144000+05	.500000+00	0	0	-1
13	1	6	5	14	.150000+20	.503000+05	.000000+00	0	0	-1
14	12	13	9	9	.136000+15	.377900+05	.000000+00	0	0	1

SAMPLE OUTPUT

ADiABATIC WELL-STIRRED REACTOR CALCULATIONS

TEMPERATURE CONSTANT

.1683+02 Time, sec

N NT IT NR KK M L NX MY MT LT

9	13	1	14	>	1	1	9	10	4	1								
H	.23/2+14	B(I)	.0000+00	BO(I)	.4297+01	-.4214+35	A(I)	.7507+03	X(I)	.0000+00								
O	.9531+34	.0000+00	.1778+00	BD(I)	.1019+33	.3153+02	.0000+00											
OH	.2584+33	.0000+00	.4311+00	.4200+14	.7773+02	.0000+00												
H ₂ O	.3524+32	.0000+00	.6611+01	.3229+37	.9223+01	.0000+00												
CH ₄	.4367+32	.1764+02	-.5185+01	-.1913+07	.1121+03	.4978+01												
CH ₃	.1529+04	.0000+00	.2930+61	-.1841+34	.5043+03	.0000+00												
CHO	.1251+06	.0000+00	.2260+03	.1258+32	.2878+03	.0000+00												
CO	.1740+33	.0000+00	.3148+C9	.6600+07	.5247+02	.0000+00												
NO	.1913+03	.0000+00	.1831+00	.10/2+07	.4822+02	.0000+00												
CO ₂	.1570+02	.0000+00	.2839+01	-.2154+37	.4354+01	.0000+00												
H ₂	.4060+04	.0000+00	.343+01	.4824+18	.1281+02	.0000+00												
O ₂	.3526+02	.7057+02	-.6398+01	.2860+35	.9744+01	.1991+00												
N ₂	.2657+31	.2662+01	-.9157+01	.3205+37	.7431+00	.7511+00												
	.3400+01	P	.2100+04	T	.5530+03	ρ_p	.3897+02	ρ_o	.2803+02	W	.2821+02	W _o	.2079+03	H	-.3110+02	H _o	.3314+00	C _p
	.5530+03	τ_R	.1000+01	X(I), b=1, NT														

ENTHALPY CONSTANT

.1617+03

ΔT_j	j=1, NR	{	.2517+01	.2295+01	.4175+01	-.5697+01	.1033+02	.1392+02	.2239+01	.2257+01	.2461+01
	.2223+01		.9909+01	-.5595+01	.1897+02	-.1769+01	.0000+00				
9	13	2	14	1	1	1	9	10			
1	IMR										
	.23/2+30+04		.000000+00		.429738+01	-.409549+03					
	.965129+34		.000000+00		.177786+00	.460556+04					
	.258387+33		.000000+00		.431071+00	.940294+04					
	.352395+02		.000000+00		.601122+01	-.205791+05					
	.436717+15		.176436+C2		-.518287+01	.510727+06					
	.152029+34		.000000+00		.293015+01	.221412+04					
	.125119+06		.000000+00		.225826+03	.196291+02					
	.174043+33		.000000+00		.314750+00	-.264277+05					
	.131269+33		.000000+00		.183084+00	.293359+03					
	.156962+02		.000000+00		.283859+01	.256725+06					
	.406019+04		.000300+00		.734249+01	-.229764+04					
	.511973+02		.705745+02		-.639766+01	.712246+05					
	.265719+01		.266226+01		-.915422+01	.293359+03					
	.3400+01		.2100+04		.5530+03	-.0000+00	.2803+02		.0000+00		
	.5530+03		.1000+01								

ENTHALPY CONSTANT

.1617+03

ΔT_j	j=1, NR	{	.2511+01	.2269+01	.4172+01	-.5693+01	.1032+02	.1397+02	.2232+01	.2253+01	.2456+01
	.2217+01		.9869+01	-.5595+01	.1894+02	-.1765+01	.0000+00				
9	13	2	14	1	1	1	9	10			
2											
	.23/2+30+04		.000000+00		.430258+01	-.417041+04					
	.979876+14		.000000+00		.17/209+00	.477585+04					
	.238424+03		.000003+00		.431167+00	.951352+04					
	.333523+17		.000003+00		.603382+01	-.206671+05					
	.436914+15		.176413+02		-.318262+01	.319611+06					
	.153512+14		.882064+02	NN	.136195+01	.494610+04					
	.125730+16		.000000+00		.226938+03	.199852+02					
	.174965+13		.000000+00		.316437+00	-.264813+05					
	.150094+13		.000000+00		.182403+03	.292574+03					
	.157712+02		.000000+00		.285233+01	.255510+06					
	.437915+14		.000000+00		.737728+01	.234610+04					
	.350503+32		.0/5651+02		-.642296+01	.711912+05					
	.285585+31		.266190+01		-.912317+01	.292576+05					
	.3400+01		.2100+04		.5529+03	-.0000+00	.2802+02		.0000+00		
	.5529+03		.1000+01								

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13. ABSTRACT

An efficient method is presented for calculating chemical composition in a perfectly stirred reactor at a given pressure, stoichiometry, and mass flow per unit volume. Either temperature or enthalpy may be prescribed as the additional condition for the computations. By employing linearization techniques, the nonlinear equations of detailed finite rate chemical kinetic schemes are reduced to a system of algebraic equations which are solved iteratively. No difficulties are experienced in obtaining converged solutions using the techniques described in this report. A computer program is presented for solution of problems with arbitrary fuel/oxidant combinations.

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